VOL. XLIII. JANUARY, 1910. NO. 1.

AMERICAN CHEMICAL JOURNAL

[Contribution from the Kent Chemical Laboratory of the University of Chicago.]

ON THE BEHAVIOR OF TRIETHYLAMINE TOWARDS OXIDIZING AGENTS.

BY T. DAR JUAN.

It has long been known that ammonia can be converted, by treatment with ethyl halides, ethyl sulphate or ethyl nitrate, into a mixture of ethylated ammonium salts. According to Nef's interpretation,[1] this reaction takes place because of a union of ethylidene with ammonia,

$$CH_3.CH\langle + H—NH_2 \rightleftarrows CH_3—CH_2—NH_2, \text{ etc.};$$

furthermore, many facts show very decisively that Hofmann's reaction is reversible. We can, for example, convert tetraethylammonium chloride, by means of an excess of dry hydrogen chloride, quantitatively at 300° into ammonium chloride and four molecules of ethyl chloride,

$$(C_2H_5)_4NCl + 4HCl \longrightarrow 4C_2H_5Cl + NH_4Cl.$$

The remarkable fact that dry ethylammonium chloride gives at 300° one molecule of ethyl chloride and ammonia,

$$C_2H_5NH_3Cl \longrightarrow C_2H_5Cl + NH_3,$$

[1] Ann. Chem. (Liebig), **309**, 160–3; **318**, 2.

whereas with a soluble alkaline hydroxide, at ordinary temperature, it gives ethylamine and a metallic chloride,

$$C_2H_5NH_3Cl + KOH \longrightarrow C_2H_5NH_2 + KCl + H_2O,$$

must, in the light of Nef's work, be interpreted as follows:

The normal products of dissociation of the salt named are ethylamine and hydrogen chloride,

$$C_2H_5NH_3Cl \rightleftharpoons C_2H_5NH_2 + HCl,$$

but ethylamine is itself in turn considerably dissociated at 300° into ethylidene and ammonia,

$$C_2H_5NH_2 \rightleftharpoons CH_3CH + NH_3;$$

consequently ethylidene unites with the hydrogen chloride present to give the far more stable and less dissociated ethyl chloride. The decomposition of dry ethylammonium chloride at 300° accordingly takes place in two successive steps,[1]

$$C_2H_5NH_3Cl \rightleftharpoons C_2H_5NH_2 + HCl \longrightarrow$$
$$C_2H_4 + NH_3 + HCl \longrightarrow C_2H_5Cl + NH_3.$$

An entirely analogous interpretation obviously holds for the transformation referred to above of tetraethylammonium chloride into ethyl and ammonium chlorides by dry hydrogen chloride.

It was now also possible, in the light of these new views, for me to begin, under Dr. Nef's guidance and direction, a systematic study of the behavior of the substituted ammonias towards oxidizing agents.

There are two ways, theoretically, in which an oxidizing agent may act upon triethylamine, for example; first, the active molecules of this substance may unite directly with oxygen to give the oxide,

$$(1) \quad (C_2H_5)_3N\langle + 2(OH) \longrightarrow (C_2H_5)_3N(OH)_2 \longrightarrow$$
$$(C_2H_5)_3N{=}O + H_2O,$$

which must then be further oxidized to nitric and acetic acids; second, only the ethylidene molecules, present in very small concentration at ordinary temperature in triethylamine,

[1] Ann. Chem. (Liebig), **309**, 163.

(2) $(C_2H_5)_3N \rightleftarrows C_2H_4 + NH(C_2H_5)_2 \rightleftarrows 2C_2H_4 + NH_2C_2H_5 \rightleftarrows 3C_2H_4 + NH_3$,

may act with the oxidizing agent present to give acetaldehyde and the products of its further oxidation, leaving therefore free ammonia as such. Assuming for a moment that the oxidation could be carried out so that the ammonia set free according to (2) remains unaltered, it would then obviously be possible to determine exactly the percentage of oxidation proceeding according to (1) and (2), respectively.

Now we know from qualitative and preliminary experiments of Carstanjen,[1] as well as of Claisen and Wallach,[2] that the ethylated ammonias give in the cold, with aqueous potassium permanganate, large amounts of acetic acid as well as free ammonia, indicating therefore that the oxidation according to (2) must be the chief one. I have therefore repeated these experiments with great care and have determined quantitatively the amounts of acetic, carbonic, oxalic and nitric acids, as well as of ammonia, which are formed under various conditions, from known amounts of triethylamine and permanganate, at 20° to 100°. Since, however, recent experiments by Herschkowitsch[3] show that ammonia itself is slowly converted by alkaline or aqueous potassium permanganate into nitrogen, as well as into nitric acid, my results prove only that the main oxidation of triethylamine proceeds according to (2); they are as yet inadequate in enabling us to decide what percentage of the oxidation (if any) proceeds according to reaction (1).

The carbon atoms in triethylamine are converted quantitatively into three molecules of acetic acid when aqueous permanganate only is used; if, however, potassium hydroxide is also simultaneously present, carbonic and oxalic acids also appear (in large amounts, the greater the concentration of the alkali) besides acetic acid. This result is self-evident in view of the recent work of Miss Denis,[4] who has proved that

[1] J. prakt. Chem., **89**, 486.
[2] Ber. d. chem. Ges., **8**, 1237.
[3] Z. physik. Chem., **68**, 93.
[4] THIS JOURNAL, **38**, 561.

acetaldehyde, formed through the oxidation of ethylidene (in ether and alcohol), gives large amounts of carbonic and oxalic acids when oxidized with alkaline permanganate, owing to an intermediate formation and oxidation of vinyl alcohol and diose.

Triethylamine and Permanganate.—An aqueous solution containing 3 grams of triethylamine was treated with 593 cc. normal potassium permanganate solution. Complete decolorization took place after standing twenty-four hours in the cold; small amounts of permanganate were now added and the solution was finally heated in a bath kept at 100° and under a reflux condenser which was connected with a receiver containing hydrogen chloride to prevent loss of ammonia. It was found that a total of 808 cc. permanganate solution was needed before the solution finally became practically decolorized on long boiling. A known quantity of potassium hydroxide was now added and the ammonia present in the aqueous solution was then driven out by hard boiling (in a bath kept at 120°) and collected in a receiver containing an excess of hydrogen chloride. The weight of ammonium chloride obtained on evaporating the acid solution on a water bath was 0.8 gram, which is 50.4 per cent. of the calculated amount; the salt obtained was proved to be free from traces of ethylated ammonium chlorides, as it sublimed without melting and gave, on digestion with alcohol, no easily soluble and low-melting salts.

The original alkaline solution was then filtered from the insoluble manganese dioxide and treated with the calculated amount of hydrogen chloride. The carbon dioxide thus set free was then determined quantitatively in the usual manner by expulsion and absorption in an aqueous solution of barium hydroxide.[1] The aqueous distillates (free from hydrochloric acid), on removal of water and volatile acids by fractionating at reduced pressure and heating finally up to 100°, were found to contain both nitric and acetic acids; after titrating an aliquot portion with 0.1 N potassium hydroxide solution the main portion of the distillate was neturalized with caustic

[1] This Journal, **38**, 561.

potash. Since potassium acetate is easily soluble in cold absolute alcohol and potassium nitrate practically insoluble in this solvent, a separation of the two salts could easily be accomplished; the potassium acetate was then converted into silver acetate which was analyzed. Thorough extraction with ether of the original salt residue gave finally, after removal of the volatile acids by distillation as stated, any oxalic acid formed in the oxidation process.

The total volume of aqueous distillate was 2 liters; 100 cc. of this required 38.2 cc. 0.1 N potassium hydroxide solution for neutralization; treatment of the remainder with 0.1 N caustic potash, etc., gave a total of 6.9 grams potassium salt (acetate) soluble in alcohol and 0.65 gram potassium nitrate; the former salt, treated in aqueous solution with silver nitrate, gave 10.5 grams of crystallized silver acetate, corresponding to 6.165 grams potassium acetate, or 3.775 grams acetic acid, *i. e.*, 70.7 per cent. of the amount theoretically possible.

0.3107 gram salt gave, on ignition, 0.2005 gram Ag.

	Calculated for $C_2H_3O_2Ag$.	Found.
Ag	64.66	64.52

No trace of oxalic or of carbonic acid was obtained in the experiment.

Triethylamine and Alkaline Permanganate.—Two experiments were carried out with 10 and 20 molecules of potassium hydroxide, respectively. In the first one a mixture of 4 grams triethylamine and 22 grams potassium hydroxide, in a small amount of water, was treated with one liter of normal potassium permanganate solution; it was found necessary to add 0.15 gram more triethylamine in order to entirely decolorize the permanganate on the boiling water bath. The amount of ammonium chloride obtained was 1.8 grams, or 82 per cent. of the calculated amount; 1.2 grams of crystallized oxalic acid melting from 99°–100° or, after loss of water of crystallization, from 186°–187°, and 1.181 gram carbon dioxide were formed from the 4.15 grams of triethylamine.

The volume of the aqueous distillate was 2.5 liters; 100

cc. required 35.4 cc. 0.1 N caustic potash for neutralization; the total amount of potassium nitrate obtained was 0.46 gram; the potassium acetate 9.83 grams, giving, by double decomposition, 14 grams of crystallized silver acetate, corresponding to 5.032 grams of acetic acid.

0.2532 gram of the silver acetate gave, on ignition, 0.1637 gram Ag.

	Calculated for $C_2H_3O_2Ag$.	Found.
Ag	64.66	64.66

In the second experiment, where 4 grams of triethylamine, 44 grams of potassium hydroxide and 1 liter of permanganate solution were used, decolorization took place after standing 8 hours in the cold; it was finally found necessary to add 260 cc. more of the oxidizing agent to complete the reaction at 100°. The amount of ammonium chloride obtained was 1.72 grams, or 81.3 per cent.; carbon dioxide, 2.418 grams; crystallized oxalic acid, 1.6 grams. The aqueous distillate (volume 2.500 cc., 100 cc. requiring 31.24 cc. 0.1 N potassium hydroxide solution) gave, on neutralization, 0.44 gram of potassium nitrate and 8.2 grams potassium acetate, which was converted in the usual manner into 12.22 grams crystallized silver acetate corresponding to 4.39 grams acetic acid.

It will be noticed that decidedly more ammonia, over 80 per cent. of the calculated amount, is formed when caustic alkali is present as well as the oxidizing agent; that carbon dioxide and oxalic acid also appear under these conditions, thus diminishing the amount of acetic acid formed, which is, however, still the main oxidation product. Finally, it should be stated here that no experiments were carried out with mono- and diethylamine, which are evidently intermediate products in the conversion of triethylamine into acetic acid and ammonia by neutral permanganate. Strangely enough, however, it was found that tetraethylammonium hydroxide is not perceptibly oxidized by long boiling either with neutral or alkaline permanganate solution.

The writer wishes to express his thanks to Professor Nef for his guidance and direction in this work.

[Contribution from the Chemical Laboratory of Harvard College.]

ON THE ACTION OF ACETIC ANHYDRIDE ON THE OCTOBROMORTHOQUINO-1-METHOXY-1'-HYDROXY-1-PHENYLENE MONOXIDE.

By C. Loring Jackson and H. A. Flint.

Many experiments have been tried in this laboratory on the action of acetic anhydride with the α-bodies, octobrom-*o*-quino-1-alkoxy-1'-hydroxy-1-phenylene monoxide,

$$C_6Br_4O(OR)\text{–}O\text{–}(HO)OC_6Br_4$$

(in which R represents the alkyl radical), made by allowing an alcohol to stand with the tetrabrom-*o*-benzoquinone in the cold. Special attention has been given to these reactions because in the earliest work[1] on this subject it was found that the α-benzyl compound, when warmed for a short time from 60° to 70° with acetic anhydride, was converted into the β-compound, octobrom-1-benzyloxy-1'-hydroxy-1,2,2-phenylene trioxide,

$$C_6Br_4(OC_7H_7)O_3(HO)C_6Br_4,$$

and the hexabrom-*o*-quinopyrocatechin ether,

$$C_6Br_4O_2C_6Br_2O_2;$$

and this reaction was used later[2] in determining the constitution of the α- and β-compounds. In the earlier experiments the β-benzyl compound, when boiled with acetic anhydride for 4 or 5 hours, was decomposed instead of giving the expected acet compound, but afterward H. A. Carlton and one of us[3] succeeded in preparing this acet derivative by boiling the β-compound with acetic anhydride for only 15 minutes, whereas, if the boiling was continued for 6 hours, a charred mass was formed, from which only a few brown needles could be extracted.

Finally, in the paper in which the constitution of the α- and β-compounds was worked out, R. D. MacLaurin and one

[1] Jackson and Porter: This Journal, **31**, 103 (1904).
[2] Jackson and MacLaurin: *Ibid.*, **37**, 92 (1907).
[3] *Ibid.*, **34**, 440 (1905).

of us described some preliminary experiments[1] on the action of acetic anhydride in the cold on the α-methyl compound, which yielded after several hours a yellow substance melting at 225° and a white one melting at 218°. No work was done on the latter, but the yellow product contained an amount of bromine corresponding to that in the α-body, and, as it seemed to be a definite compound, it was suggested that it might belong to a third (γ) class. With warm acetic anhydride Dr. MacLaurin obtained products melting at 138°–140° and at 195° with the hexabrom-*o*-quinopyrocatechin ether.

These earlier experiments gave results which invited further study, and in this paper we describe an investigation of Dr. MacLaurin's yellow product. This we prepared by allowing the acetic anhydride to act on the α-body for a week or 10 days instead of a few hours. The product obtained under these conditions showed the constant melting point 244° instead of 225°, as observed by Dr. MacLaurin in his preliminary experiments. This difference in the two results is not hard to understand; the melting is accompanied by decomposition, and in these cases the temperature is much influenced by the conditions of heating, so that constant results can be obtained only when these conditions are the same, and two different observers might well find melting points many degrees apart, showing a difference even as large at 19°. It is also possible that the product of Dr. MacLaurin's preliminary experiments contained a persistent impurity of the unchanged α-compound, and this supposition is in harmony with the fact that he allowed the action of the acetic anhydride to proceed only for a few hours, whereas we found at least a week was necessary to complete it.

The melting point 244° suggested at once that the substance was the heptabrom-*o*-quinopyrocatechin hemiether,

$$C_6Br_4(OH)OC_6Br_3O_2,$$

and this was proved to be the case by its analysis and its other properties. This substance oddly enough contains the same amount of bromine as the α-methyl compound, but the de-

[1] This Journal, **37**, 103 (1907).

terminations of carbon and hydrogen proved that it has a different composition. The formation of the heptabrom hemiether would indicate that the acetic anhydride had decomposed the α-body completely into two molecules of tetrabrom-*o*-quinone and methyl alcohol (or more probably acetate), and that one of these quinones had then undergone a reduction to tetrabrompyrocatechin, which afterward combined with the remaining quinone with loss of hydrobromic acid. The hexabrom-*o*-quinopyrocatechin ether obtained by Dr. Porter from the α-benzyl compound and hot acetic anhydride must have been formed in a similar way. It is certainly strange that compounds so stable as these toward other reagents should be decomposed by acetic anhydride, but as stated earlier the fact has been observed repeatedly in this laboratory.

In our experiments, which were carried on for a longer time than Dr. MacLaurin's, none of his white product was obtained so we are unable to give any account of this body, and our experiments with warm acetic anhydride apparently ran beyond the low-melting products found by him, as we obtained the heptabrom hemiether, $C_6Br_4(OH)OC_6Br_3O_2$, and the hexabrom ether, $C_6Br_4O_2C_6Br_2O_2$.

The further study of the reactions of acetic anhydride with the α-bodies will be carried on in this laboratory.

EXPERIMENTAL.

The tetrabrom-*o*-benzoquinone used was prepared by the method described by us in a previous paper.[1] The method[2] for preparing the α-compound was improved by putting the mixture of 50 grams of tetrabrom-*o*-quinone and 100 cc. of methyl alcohol in a glass-stoppered bottle on the shaking machine, when the reaction was complete in six or seven days, thus saving from one-third to one-half the time required when the mixture was allowed to stand at rest as in the earlier method.

Ten grams of the α-compound, $(C_6Br_4O_2)_2CH_3OH$, mixed with 80 cc. of acetic anhydride, were shaken for 15 minutes

[1] THIS JOURNAL, **39**, 83 (1908).

[2] Jackson and Porter: *Ibid.*, **31**, 95 (1904). Jackson and Carlton: *Ibid.*, **34**, 425 (1905).

and then allowed to stand with only occasional shaking at ordinary temperatures for a week or 10 days, that is, until the white color of the original substance had been completely replaced by yellow. The product was then filtered out, washed with gasoline, and recrystallized from a mixture of benzene and gasoline, until it showed the constant melting point 244°, when it was dried *in vacuo* for analysis:

I. 0.2172 gram substance gave 0.1466 gram CO_2 and 0.0077 gram H_2O.

II. 0.3762 gram substance gave 0.2650 gram CO_2 and 0.0142 gram H_2O.

III. 0.1432 gram substance gave 0.2452 gram AgBr.

IV. 0.1456 gram substance gave 0.2496 gram AgBr.

V. 0.1515 gram substance gave 0.2585 gram AgBr.

	Calculated for $C_6Br_4OHOC_6Br_3O_2$.	Found.				
		I.	II.	III.	IV.	V.
C	18.73	18.41	19.21	...	...	...
H	0.13	0.39	0.42	...	...	...
Br	72.81	...	...	72.86	72.97	72.63

The substance is therefore the heptabrom-*o*-quinopyrocatechin hemiether, and this is confirmed by its melting at 244° with the formation of a red liquid, and the fact that, when crystallized from a solvent containing benzene, it appears in the very characteristic square plates of a brilliant yellow color, which effloresce on exposure to the air. Warm alcohol converts it into the hexabrom-*o*-quinopyrocatechin ether, and its solubilities are the same as those of the heptabrom compound.

To study the action of hot acetic anhydride 2 grams of the α-body were dissolved in 30 cc. of acetic anhydride and warmed on the steam bath for half an hour, after which the addition of 500 cc. of water precipitated a pale reddish substance. Ether extracted from this a quantity of the heptabrom-*o*-quinopyrocatechin hemiether, identified by its melting point and properties, and left behind a red body, which did not melt below 300°, was essentially insoluble in all the common solvents, but could be crystallized from nitrobenzene, and was therefore undoubtedly the hexabrom-*o*-quinopyrocatechin

ether, $C_6Br_4O_2C_6Br_2O_2$. The acetic anhydride in this experiment behaved in the same way as it did when acting in the cold, the hexabrom compound being undoubtedly formed from the heptabrom hemiether, which was the first product.

In a preliminary experiment a few grams of heptabrom-*o*-quinopyrocatechin hemiether were shaken for 8 hours with a 10 per cent. solution of sodic hydrate. The product formed white rhombic crystals and melted with decomposition at about 240°. It was remarkable, because it gave so faint a test for halogen on copper wire that it seemed to be free from bromine. It will be investigated further.

CAMBRIDGE, October 27, 1909.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXVI.—RESEARCHES ON HALOGENAMINO ACIDS: THE POSITION OF THE IODINE ATOMS IN DI-IODTYROSINE (IODGORGOIC ACID).

[EIGHTH PAPER.]

BY HENRY L. WHEELER AND CARL O. JOHNS.

Diiodtyrosine was first prepared synthetically by Wheeler and Jamieson.[1] Our work at that time served to show that this substance is identical with iodgorgoic acid, which Drechsel[2] obtained by the hydrolysis of a Mediterranean coral (*Gorgonia Cavolini*).

It has not hitherto been determined in what part of the molecule the iodine atoms are located. From the fact that halogens attack phenols in the ortho, in preference to the meta positions, we suggested that the compound was 3,5-diiodtyrosine. Since then this substance has been referred to by various writers as 3,5- and also, without adequate reason, as 2,5-diiodtyrosine.

In this paper we describe the results of our work, which now conclusively prove that the iodine atoms in diiodtyrosine are attached in the 3- and 5-positions. It has been found by Dr.

[1] THIS JOURNAL, **33**, 365 (1905)
[2] Z. Biol., **33**, 90 (1896).

S. H. Clapp, working with one of us, that diiodtyrosine can easily be methylated by means of methyl iodide and potassium hydroxide. When this methylated product, which is provisionally[1] represented by formula II, was boiled with sodium hydroxide a sodium salt of an acid free from nitrogen was obtained. This acid, moreover, contained iodine and, on analysis, gave results agreeing with those calculated for a diiod-*p*-methoxycinnamic acid (III).

A similar behavior has apparently been observed in the case of tyrosine. Körner and Menozzi[2] found, on methylating tyrosine, that a compound represented by the formula

$$CH_3OC_6H_4C_2H_3(CO_2K)N(CH_3)_3I,$$

was obtained. When this was warmed with alkali *p*-cumaric acid was formed. This paper is inaccessible to us at present. We have now prepared 3,5-diiod-*p*-methoxycinnamic acid (III) from material which has been proved by us to have the halogen in the 3- and 5-positions and we find that this synthetic preparation and that obtained from diiodtyrosine by degradation (*Abbau*) are identical. 3,5-Diiod-*p*-methoxycinnamic acid (III) was prepared by methylating the diiod-*p*-hydroxycinnamic acid (V) of Paal and Mohr.[3] This process gave a mixture of the acid (III) and the methyl ester (IV).

The diiod-*p*-hydroxycinnamic acid was prepared from diiod-*p*-hydroxybenzaldehyde (VI), which, in turn, was obtained by iodating *p*-hydroxybenzaldehyde as described by Paal.[4] Paal and Mohr state that by oxidizing this diiod aldehyde the *m*-diiod-*p*-hydroxybenzoic acid (VII) of Peltzer[5] smoothly results and that therefore the constitution is established.

A search through Peltzer's article failed to reveal any proof or mention whatever of the position of the halogen in his acid. In fact he tried to determine the structure of the acid by heating with soda, in the hope of obtaining gallic acid or an isomer.

[1] Owing to the departure of Dr. Clapp before the work was finished, a description of the methylated product is reserved for a later paper.

[2] Gazz. Chim. Ital., **11**, 550; Beilstein's Handbuch, [3] **2**, 1569.

[3] Ber. d. chem. Ges., **29**, 2306 (1896).

[4] *Ibid.*, **28**, 2412 (1895).

[5] Ann. Chem. (Liebig), **146**, 294 (1868).

His attempts were, however, unsuccessful. No other work on this acid being known to us, it was necessary to establish the structure of this compound.

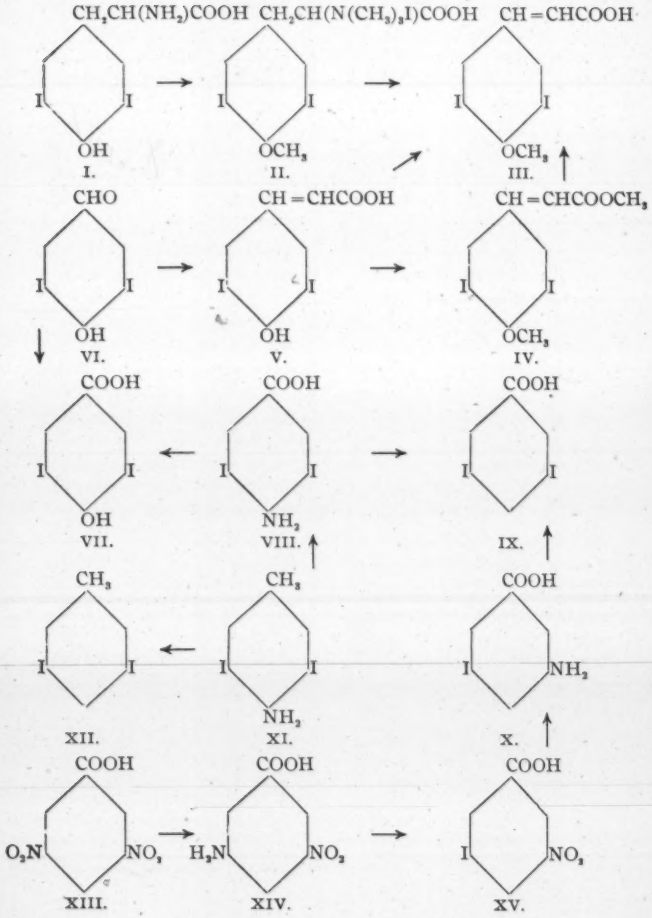
The proof that the iodine atoms are in the 3,5-positions in diiod-*p*-hydroxybenzoic acid was obtained by Wheeler and Liddle[1] by converting the 3,5-diiod-*p*-aminobenzoic acid (VIII) into the hydroxy acid in question. This acid was first prepared by Michael and Norton.[2] They did not prove, but, here again, assumed as most probable, that the iodine atoms were in the 3,5-positions.

This diiodamino acid (VIII), however, has been shown by Wheeler and Liddle to be a 3,5-diiod derivative. Its structure was established in two different ways.

In the first case it was obtained by oxidizing the acetyl derivative of 3,5-diiod-*p*-toluidine (XI) which, on diazotizing and removing the amino group, gave 3,5-diiodtoluene (XII). In the second case the diiodamino acid was converted by the diazo reaction into a diiodbenzoic acid (IX), which was found to be identical with 3,5-diiodbenzoic acid prepared from Hübner's 3,5-dinitrobenzoic acid (XIII). The nitro groups in the latter compound were alternately reduced and replaced by iodine. In this manner we obtained 3-nitro-5-aminobenzoic acid (XIV), 3-nitro-5-iodbenzoic acid (XV), 3-amino-5-iodbenzoic acid (X), and finally 3,5-diiodbenzoic acid (IX).

These results settle the structure of diiodtyrosine. They also settle the structure of the other compounds which were previously assumed to be 3,5-diiod derivatives. The formulas and the relations of the substances may be represented as follows:

[1] THIS JOURNAL, **42**, 441 (1909).
[2] *Ibid.*, **1**, 264 (1879).


CH2CH(NH2)COOH
CH2CH(N(CH3)3I)COOH
CH=CHCOOH
OH
I.
OCH3
II.
OCH3
III.
CHO
CH=CHCOOH
CH=CHCOOCH3
OH
VI.
OH
V.
OCH3
IV.
COOH
COOH
COOH
OH
VII.
NH2
VIII.
IX.
CH3
CH3
COOH
NH2
XII.
NH2
XI.
X.
COOH
COOH
COOH
O2N
NO2
XIII.
H2N
NO2
XIV.
NO2
XV.

EXPERIMENTAL PART.

3,5-Diiod-p-*methoxycinnamic Acid from Diiodtyrosine.*—The tyrosine used was prepared from silk and casein by hydrolysis with dilute sulphuric acid in the usual manner. This was converted into diiodtyrosine in the manner described by Wheeler and Jamieson. It was purified by recrystallizing from water.

Two and seven-tenths grams of pulverized diiodtyrosine were suspended in about 80 cc. of methyl alcohol and 1.8 grams, or 5 molecular proportions, of potassium hydroxide were added. The acid quickly dissolved, forming a bright red solution. Eight grams of methyl iodide (the calculated amount for 5 molecules is 4.4 grams) were added and the solution was boiled for seven and a half hours in a flask attached to a return condenser. Crystalline material separated which was probably potassium iodide. The solution was evaporated to dryness and the residue was stirred and digested with cold water. The material left undissolved by this treatment then weighed 3.2 grams. This yield is more than the calculated for a simple methyl derivative. The calculated amount for a dimethylamino-*p*-methoxy methyl ester or a tetramethyl derivative is 3.04 grams. The calculated weight for a trimethyl ammonium iodide of the *p*-methoxy acid (II) is 3.84 grams.

This material dissolved easily in dilute alkali and readily in ethyl alcohol. It melted under the alcohol when warmed and it separated from a small volume of the solution in an amorphous condition. The whole was warmed with dilute sodium hydroxide. The solution had a strong odor of amine from the start and, after warming for 6 hours, concentrating, and cooling, shining scales or plates separated. Hydrochloric acid was added in slight excess. This produced an amorphous precipitate which weighed 2 grams. The calculated yield from a methoxytrimethylammonium iodide is 2.2 grams. This substance was practically insoluble in water and very soluble in methyl alcohol, and separated, on extreme concentration, in fine, small prisms. It was purified for analysis by dissolving in ethyl alcohol and precipitating with hot water. It separated in aggregates of minute prisms which melted at about 200° (Analysis I).

In another experiment, 5.4 grams of diiodtyrosine was methylated as above. The solution was boiled for 20 hours, the proportions used being 3.6 grams of potassium hydroxide, 100 cc. of methyl alcohol and 15 grams of methyl iodide. The product obtained was boiled with dilute sodium hydroxide, concentrated, and the crystalline sodium salt was filtered off, dissolved in water and the acid precipitated with hydrochloric acid. This preparation was used for comparison with that obtained by the following method:

*3,5-Diiod-*p*-methoxycinnamic Acid from 3,5-Diiod-*p*-hydroxybenzaldehyde.*—Nine grams of *p*-hydroxybenzaldehyde gave, by Paal's method, 23.7 grams of diiod-*p*-hydroxybenzaldehyde melting at 198°, and 16.5 grams of this gave, by Perkins' synthesis, when carried out as described by Paal and Mohr, 11.1 grams of 3,5-diiod-*p*-hydroxycinnamic acid. The acid melted with decomposition at 247°. The above authors give 245°. Six grams of 3,5-diiod-*p*-hydroxycinnamic acid, 4.1 grams of potassium hydroxide in a few cc. of water, and 15 grams of methyl iodide were mixed in 100 cc. of methyl alcohol. The clear solution was allowed to stand overnight and was then warmed on the steam bath until it was no longer alkaline. The methyl alcohol was removed by evaporating to dryness and the residue was treated with water. A part dissolved and the insoluble portion was thoroughly washed with water. It weighed 2.8 grams and proved to be the methyl ester of 3,5-diiod-*p*-methoxycinnamic acid (see below).

On adding hydrochloric acid to the aqueous filtrate an amorphous white precipitate separated. This weighed 2.7 grams and when it was crystallized from 25–30 cc. of 95 per cent. alcohol it formed knobs or hard balls of minute prisms which melted quite sharply and completely at 198°–199°. An iodine determination agreed with the calculated value for 3,5-diiod-*p*-methoxycinnamic acid (Analysis II).

	Calculated for $C_{10}H_8O_3I_2$.	Found. I.	II.
I	59.07	59.21	58.96

This acid is practically insoluble in water, but readily soluble in methyl or ethyl alcohol. It separates from its solution

in alkalies on acidifying as a bulky, amorphous white precipitate, which becomes more compact on warming. It was found that chloroform was the best solvent to use for the purification of the substance. It is only moderately soluble in chloroform, from which it separates in the form of beautiful, long, silky needles. These melted constantly at 202°–203°. The acid melting at about 200°, obtained by Mr. Clapp from diiodtyrosine, was also crystallized from chloroform, whereupon the same long, silky needles melting at 202°–203° were obtained. When portions of the two samples were mixed the melting point was not altered.

The sodium salt and the methyl ester are the most characteristic derivatives of the acid.

The *Sodium Salt*, $CH_3OC_6H_2I_2CH=CHCOONa$. — Three grams of the acid were dissolved, by boiling, in 15 cc. of water containing 0.3 gram of sodium hydroxide; on cooling, a thick or bulky mass of very thin, pearly plates, or scales, was obtained. The mass was so thick that the test tube could be inverted without loss of the contents. The crystals were filtered off and recrystallized from water. They were very soluble in hot and only moderately soluble in cold water. They lost one per cent. of water at 110°, after drying over sulphuric acid for 2 days. A sodium determination gave:

	Calculated for $C_{10}H_7O_3I_2Na$.	Found.
Na	5.08	4.89

The *potassium salt* was found to be far more soluble than the sodium salt.

The *barium salt* formed a white, bulky precipitate when barium chloride was added to an aqueous solution of the sodium salt. It was difficultly soluble in boiling water and it crystallized in long, colorless needles.

The *silver salt*, prepared by adding silver nitrate to a solution of the sodium salt, was an amorphous white precipitate. It was insoluble in hot water and it did not darken when exposed to light for several days.

The *mercury salt*, from mercuric chloride and the potassium salt, formed a gelatinous precipitate insoluble in hot water.

The *copper salt* was obtained as an amorphous, light green precipitate on adding copper sulphate to a solution of the sodium salt. It was insoluble in hot water.

The *Methyl Ester of 3,5-Diiod*-p-*methoxycinnamic Acid*, $CH_3OC_6H_2I_2CH=CHCOOCH_3$.—As mentioned above, this ester was obtained, along with 3,5-diiod-*p*-methoxycinnamic acid, when 3,5-diiod-*p*-hydroxycinnamic acid was methylated with potassium hydroxide and methyl iodide. It is far less soluble in alcohol than the methoxy acid. While 2.7 grams of the acid dissolved in 25–30 cc. of alcohol, it required, on the other hand, about 200 cc. of hot 95 per cent. alcohol to dissolve 2.8 grams of the methyl ester. On cooling, very thin, elongated, shining, twinned plates were obtained. They were insoluble in water and melted to a clear, yellow oil at 173°–174°.

	Calculated for $C_{11}H_{10}O_3I_2$.	Found.
I	57.20	57.40

This same ester was obtained on esterifying the diiod-*p*-methoxycinnamic acid prepared from diiodtyrosine. Seven-tenths gram of the acid obtained by Mr. Clapp was dissolved in 25 cc. of methyl alcohol, 2 drops of concentrated sulphuric acid were added, and the solution was boiled for two hours. During the course of the reaction crystals separated and, on cooling, 0.5 gram of thin plates was obtained. These melted at 173°–174° and when mixed with the above sample the melting point was not altered. The two preparations were identical in every respect.

The *Ethyl Ester of 3,5-Diiod*-p-*methoxycinnamic Acid*, $CH_3OC_6H_2I_2CH = CHCOOC_2H_5$.—One gram of the acid was dissolved in 50 cc. of absolute alcohol containing 5 drops of concentrated sulphuric acid and the solution was boiled for 3 hours. As nothing separated the solution was evaporated to about 30 cc. whereupon, on cooling, 0.85 gram of crystals separated. They were recrystallized from alcohol and thus obtained in small, stout, colorless prisms which grew in fern-like clusters. This ester melted to a clear oil at 135° and was easily soluble in chloroform, difficultly soluble in alcohol, and insoluble in water. An iodine determination gave a re-

sult agreeing with the calculated value for ethyl 3,5-diiod-*p*-methoxycinnamate.

	Calculated for $C_{12}H_{12}O_3I_2$.	Found.
I	55.46	55.43

NEW HAVEN, CONN.,
June, 1909.

[Contributions from the Sheffield Laboratory of Yale University.]

CLXXVII.—RESEARCHES ON PYRIMIDINES: THE THIO DERIVATIVES OF THYMINE AND THE PREPARATION OF THYMINE.[1]

[FORTY-NINTH PAPER.]

BY HENRY L. WHEELER AND DAVID F. MCFARLAND.

In preparing uracil from ethylpseudothiourea hydrobromide and the sodium salt of ethyl formylacetate,[2] for some unknown reason it has sometimes happened that the yield obtained was very poor. A more satisfactory result was invariably obtained when sodiumformylacetate and thiourea were used.[3] The employment of thiourea instead of the pseudothiourea had the additional advantage of being a more direct process. It rendered unnecessary the preparation of the pseudothiourea and was therefore less expensive, and, perhaps better than all, the presence of mercaptan was avoided.

These results suggested that the preparation of thymine might be improved in a similar manner. When the sodium salt of ethyl formylpropionate was condensed with thiourea in aqueous solution (four experiments) we were surprised to find that the yield of 2-thiothymine (I) was invariably about one-half what would be expected from the pseudothiourea condensation under similar conditions. Obviously this was no improvement over our original method.

We have recently found, in other cases, that certain β-ketone esters condense with thiourea in alcoholic solution when they

[1] Part of a thesis presented by David F. McFarland for the degree of Ph.D., Yale, 1909.

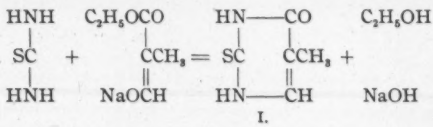
[2] Wheeler and Merriam: THIS JOURNAL, **29**, 478 (1903).

[3] Wheeler and Liddle: *Ibid.*, **40**, 547 (1908).

failed to do so in water. The condensation of ethyl sodiumformylpropionate with thiourea was therefore carried out in alcoholic solution (eight experiments). This brought about the desired improvement. The yields were over twice those obtained in the aqueous condensation.

For comparison with our original method ethyl sodiumformylpropionate was condensed with ethylpseudothiourea in aqueous (four experiments) and alcoholic (one experiment) solutions. It was then found that the average yield of 2-ethylmercapto-5-methyl-6-oxypyrimidine, in these experiments, when expressed in the equivalent weight of thymine, was nearly identical (20.9 per cent. of the calculated) with that calculated from the average yield of 2-thiothymine obtained in the alcoholic condensations (22.6 per cent. of the calculated).

In other words, almost the same amount of thymine is obtained in these condensations whether we use thiourea in alcohol or pseudothiourea in water or alcohol. The use of thiourea, however, gives a little better yield and it is also to be recommended for the reasons stated above. The condensation takes place as follows:



I.

It is peculiar that a similar condensation failed to take place in the case of urea and ethyl sodiumformylpropionate or ethyl sodiumformylacetate[1] in either absolute alcohol or aqueous solutions.

2-Thiothymine (I), like 2-thiouracil, is desulphurized and quantitatively converted into thymine (V) by simply dissolving in water and evaporating to dryness with a slight excess of chloracetic acid. The thymine prepared in this manner

[1] Wheeler and Liddle: *Loc. cit.*

melts higher and appears to be more readily purified than when prepared by means of a pseudothiourea.

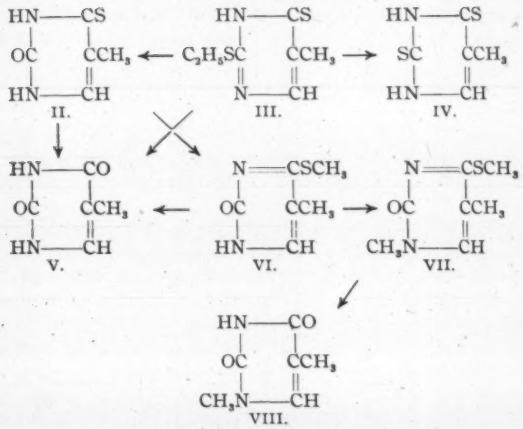
We have prepared 6-thiothymine (II) and 2,6-dithiothymine (IV) in a manner similar to that used in the case of the corresponding uracil[1] and 4-methyluracil derivatives.[2] The preparation of the 6-thio derivatives in the thymine series is far less satisfactory than in the case of those previously described. The 2-ethylmercapto-5-methyl-6-thiopyrimidine (III), on boiling with hydrochloric acid, evolves mercaptan less easily than in the previous cases and the sulphur in the 6-position is also more or less removed at the same time, so that the yield is poor, or nothing but thymine is obtained. A similar behavior was observed in the preparation of 6-thiouracil but only on long warming with acid. On the other hand, 6-thio-4-methyluracil evolved mercaptan smoothly without being desulphurized in the 6-position.

2,6-Dithiothymine (IV) was prepared from 2-ethylmercapto-5-methyl-6-thiopyrimidine (III) by heating with dry hydrogen chloride.

We have found that the methylation of 6-thiothymine first gives 2-oxy-5-methyl-6-methylmercaptopyrimidine (VI), as would be expected, and on further methylation this compound yields the 3-methyl derivative, 2-oxy-3,5-dimethyl-6-methylmercaptopyrimidine (VII). This result is in accordance with the general tendency, previously observed by us, of a 6-mercapto-2-oxypyrimidine to alkylate in the 3-position.

2-Oxy-3,5-dimethyl-6-methylmercaptopyrimidine (VII), on boiling with hydrochloric acid, gives a quantitative yield of 3-methylthymine (VIII). These compounds and their transformations may be represented as follows:

[1] Wheeler and Liddle: *Loc. cit.*
[2] Wheeler and McFarland: THIS JOURNAL, **42**, 431 (1909).



EXPERIMENTAL PART.

Ethyl Sodiumformylpropionate, $NaOCH=C(CH_3)CO_2C_2H_5$.—This salt was prepared, as Wislicenus directs,[1] in a manner similar to that used in the case of ethyl sodiumformylacetate. We have obtained the best results in the preparation of these salts when one atomic proportion of sodium was covered with dry ether in a flask attached to a return condenser and the mixture of esters slowly added. An excess of ethyl formate was employed and the amount of ether was sufficient to prevent the mixture from becoming thick. Three or four times the volume of the mixed esters was usually sufficient. If evaporation of the ether took place, owing to the esters being added too rapidly, or if not enough was present, the product frequently was sticky and difficult or impossible to filter. It therefore could not be washed with ether and dried satisfactorily. When 100 to 150 grams of each ester were used about a day and a half or two days was taken to add the mixture to the sodium. The sodium disappeared and the reaction was complete in about four days altogether.

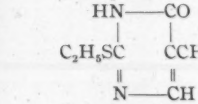
In one experiment from 150 grams of ethyl propionate and

[1] Ber. d. chem. Ges., **20**, 2934 (1887).

900 cc. of ether with one atomic proportion of sodium and 150 grams of ethyl formate, 145 grams of dry sodium salt were obtained. In the ether filtrate 9.6 grams of 2-thiothymine were found, or an equivalent of 32.3 grams more of sodium salt (see experiment XIV below). The total yield of crude sodium salt was therefore 177.3 grams for 150 grams of ethyl propionate, or 118.2 grams for 100 grams of ester.

In another experiment which was carried out in the same manner as the above, 50 grams of ethyl propionate gave 43.2 grams of dry sodium salt and an amount of 2-thiothymine (4.3 grams) in the ether filtrate (experiment XV) equivalent to 16.8 grams more of salt, making a total of 60 grams or 120 grams for 100 grams of ethyl propionate. This is 79 per cent. of the calculated. (See also experiment XIII below.) In the condensations in which we have used this crude salt, the yields of pyrimidine derivatives have in no case amounted to much over 30 per cent. of the calculated. The salt is obviously not pure, but whether or not this fact alone accounts for the low yield, or whether stereochemically different salts exist here, one form condensing and the other not, will have to be determined later.

Preparation of 2-Ethylmercapto-5-methyl-6-oxypyrimidine,[1]



—I. One hundred grams of propionic ester and 80 grams of formic ester were added to 22.5 grams of sodium covered with ether. The ethyl sodiumformylpropionate was not filtered off but was condensed with 100 grams of pseudoethylthiourea hydrobromide by means of 65 grams of potassium hydroxide in about 750 cc. of water. On acidifying with acetic acid, after warming the mixture, 33 grams of 2-ethylmercapto-5-methyl-6-oxypyrimidine melting at 150° were obtained.

II. In another experiment 150 grams of propionic ester, 120 grams of formic ester and 33.7 grams of sodium were used. The product was mixed with a solution of 150 grams of ethylpseudothiourea hydrobromide and 97 grams of potas-

[1] See Wheeler and Johnson: THIS JOURNAL, **31**, 595 (1904).

suim hydroxide in about a liter of water. The yield of mercaptopyrimidine was 57.5 grams.

III. This experiment was carried out by Dr. Victor C. Myers. One hundred and fifteen grams of propionic ester, 100 grams formic ester and 26 grams of sodium in 250 cc. of ether were taken. The sodium salt was not filtered off but was condensed with 97 grams of ethylpseudothiourea hydrobromide and 30 grams of potassium hydroxide. The solution was allowed to stand for 24 hours and then concentrated to one-half volume (300 cc.?) before precipitating with dilute acetic acid. The precipitate weighed 61.5 grams. This probably contained some potassium and sodium salts since on recrystallizing from water 40 grams of material melting at 158°–159° was obtained.

IV. The above experiment was repeated with the same quantities and under the same conditions. The first portion of mercapto compounds separated weighed 53.3 grams. When recrystallized from water 38.3 grams of pure material were obtained. The mother liquor contained sodium and potassium salts.

V. In this experiment the condensation was tried in alcohol. Thirteen and a half grams of dry ethyl sodiumformylpropionate were mixed with 16.4 grams of ethylpseudothiourea hydrobromide in 300 cc. of absolute alcohol in which 2.0 grams of sodium had been dissolved. Complete solution did not take place. The mixture was shaken and let stand for 20 hours, then warmed on the steam bath, evaporated to dryness and dissolved in 60 cc. of water and precipitated with acetic acid. The precipitate weighed 3.85 grams.

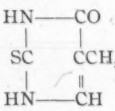
The following table gives a further comparison of the above results:

	Weight of ethyl propionate.	Weight of ethyl sodiumformylpropionate	Weight of mercapto derivative obtained.	Calculated weight of mercapto derivative per 100 grams ester.	Per cent. yield of mercapto derivative.	Calculated weight of thymine from 100 grams ester.
I	100	120[1]	33.0	33.0	19.75	24.4
II	150	180[1]	57.5	38.3	22.9	28.4
III	115	138[1]	61.5	53.3	31.9	39.5
IV	115	138[1]	53.2	46.3	27.7	34.3
V	...	13.5	3.85	33.7	20.2	24.9

[1] Calculated from average yield of salt.

If we exclude experiments III and IV, in which the results are a little too high, as already stated, the average yield of thymine is 25.9 grams from 100 grams of ethyl propionate (or including these results it is 30.3 grams). Twenty-five and nine-tenths grams of thymine is 20.9 per cent. of the theoretical amount calculated directly from the ethyl propionate.

Preparation of 2-Thiothymine,



in Alcoholic Solution.—VI. Nineteen grams of ethyl sodiumformylpropionate, pressed on paper and dried until all odor of ether had disappeared, were added to a solution of 9.5 grams (one molecule) of thiourea and 2.9 grams of sodium in 350 cc. of absolute alcohol. The mixture was warmed for 3 hours, evaporated to dryness, dissolved in 80 cc. of water and precipitated with dilute acetic acid. The crystalline precipitate weighed 6.8 grams.

VII. Twenty-eight grams of the sodium salt were warmed for five hours with 14 grams (1 molecule) of thiourea in 400 cc. of absolute alcohol, then evaporated to dryness, dissolved in water and precipitated with acetic acid. The yield in this case was 8.0 grams.

VIII. Fourteen and one-tenth grams of the dry sodium salt were treated with the same relative proportions of the thiourea, sodium ethylate, and alcohol and under the same conditions as in experiment VI. The yield of 2-thiothymine was 3.4 grams.

IX. Fifteen grams of the sodium salt, 4 grams of thiourea (about one-half molecule) and 2.2 grams of sodium dissolved in 150 cc. of absolute alcohol were mixed and heated for 3 hours. Then 25 cc. of water were added and the whole evaporated to dryness. The residue was taken up in 60 cc. of water and precipitated with acetic acid. The precipitate weighed 4.0 grams. On recrystallizing from 17.5 cc. of alcohol 3.4 grams separated.

X. Twenty-seven grams of the sodium salt were warmed with 13.5 grams (one molecule) of thiourea and 4.3 grams of sodium in 350 cc. of 95 per cent. alcohol for three and a half hours. There remained considerable material undissolved. The alcohol was evaporated and the residue was dissolved in 140 cc. of water. The addition of acetic acid to this solution gave 8.0 grams of 2-thiothymine.

XI. Thirteen and two-tenths grams of sodium salt were warmed with 3.5 grams of thiourea (a little over one-half molecule) and 2 grams of sodium in 150 cc. of 95 per cent. alcohol for 3 hours. Twenty-five cc. of water were added and the solution was warmed for a half hour, then evaporated to dryness. The residue was taken up in 60 cc. of water and precipitated, whereupon 3.3 grams of 2-thiothymine were obtained.

XII. Fifteen grams of dry sodium salt were warmed 3 hours with 4 grams of thiourea (one-half molecule + 0.5 gram) and 2.3 grams of sodium dissolved in 100 cc. of 85 per cent. alcohol. The sodium salt was first dissolved in 15 cc. of water and then the sodium ethylate and thiourea were added. Some solid separated after warming, 10 cc. more water were added and the solution heated for a half hour longer. On evaporating to dryness, dissolving in 60 cc. of water and precipitating, 3.8 grams of 2-thiothymine were obtained. On recrystallizing from 175 cc. of water 3.2 grams separated.

XIII. Fifty grams of ethyl propionate, 43.5 grams of ethyl formate and 11.3 grams of sodium gave 47.5 grams of dry ethyl sodiumformylpropionate. The ether filtrate was evaporated to dryness and the residue was combined with the above. Calculating on the basis of 65 grams of sodium salt in the entire lot, twenty grams of thiourea (over half molecule) in 500 cc. of 95 per cent. alcohol were added. The mixture was heated three and a half hours, the alcohol was then evaporated and the residue dissolved in 175 cc. of water. When precipitated as in the previous cases, 15 grams of 2-thiothymine were obtained.

XIV. The ether filtrate from a condensation in which 150 grams of ethyl propionate were converted into sodium salt

was evaporated to dryness and treated with 4 grams of sodium in 400 cc. of absolute alcohol and 20 grams of thiourea. The mixture was heated one hour on the steam bath and then evaporated to dryness. Two hundred and fifty cc. of water were added and the solution, on precipitating with acetic acid, gave 9.6 grams of 2-thiothymine. From the average yield of four condensations with the filtered salt it is calculated that the ether solution in this case contained 32.3 grams of ethyl sodiumformylpropionate.

XV. The ether filtrate from the preparation of ethyl sodiumformylpropionate in which 50 grams of ethyl propionate were used was treated as above with 3 grams of sodium in 100 cc. of absolute alcohol and 5 grams of thiourea. The mixture was warmed for 3 hours, then 35 cc. of water were added and the solution was warmed for a half hour longer. On evaporating to dryness, taking up in 50 cc. of water, and adding acetic acid 4.3 grams of 2-thiothymine were obtained.

The following table gives the results of the condensation of ethyl sodiumformylpropionate with thiourea in alcoholic solutions:

	Weight of ethyl sodiumformyl-propionate.	Number of cc. of alcohol for 1 gram of sodium salt.	Weight of 2-thio-thymine obtained.	Calculated weight of 2-thio-thymine from 100 grams ester.	Per cent. yield of 2-thio-thymine.	Calculated weight of thymine from 100 grams ester.
VI	19.0	18.4	6.8	42.3	30.4	37.6
VII	28.0	14.3	8.0	33.8	24.2	30.0
VIII	14.1	18.4	3.4	28.6	20.5	25.3
IX	15.0	10.0	4.0	32.0	23.0	28.4
X	27.0	13.0	8.0	35.0	25.1	31.0
XI	13.2	11.3	3.3	30.0	21.6	26.6
XII	15.0	5.7	3.8	30.4	21.8	27.0
XIII	60.0?	8.3	15.0	30.0	20.1	24.8

Experiments VI, VII, VIII and IX were carried out in absolute alcohol, X, XI and XIII in 95 per cent. alcohol, and XII in 85 per cent. alcohol. Experiment VIII is a duplicate of VI. Sodium ethylate and the calculated quantity of thiourea were present. Number VII was similar except that no sodium ethylate was used. In IX sodium ethylate was present but only one-half the calculated quantity of thiourea

was added. In the remaining experiments sodium ethylate and about one-half the calculated quantity of thiourea was employed, except in X, where one molecular proportion of thiourea was used.

If we exclude experiment VI, which for some unknown reason gave a much higher yield of 2-thiothymine than the others, and also experiment XIII, in which the amount of salt taken was determined by calculation, we find that the average yield of thymine by this method is 28.0 grams from 100 grams of ethyl propionate. This is 22.6 per cent. of the calculated.

Preparation of 2-Thiothymine in Aqueous Solution.—XVI. Seventeen grams of ethyl sodiumformylpropionate were dissolved in a solution of 8.5 grams (one molecule) of thiourea in 65 cc. of water. The solution was allowed to stand for 10 hours, then precipitated with acetic acid. The yield of 2-thiothymine was 2.5 grams.

XVII. (By WALTER F. STOREY.) One hundred grams of propionic ester were condensed with an excess of ethyl formate and a little over (2 grams) one atomic proportion of sodium. When all the sodium had disappeared the calculated quantity (one molecule) of thiourea was added in ice water and the mixture thoroughly shaken. After standing overnight the ether was removed and, after warming, concentrating and cooling, acetic acid was added. The yield was 14.5 grams of the thiopyrimidine.

XVIII. One hundred and fifty grams of ethyl propionate, 115 grams of ethyl formate and 36 grams instead of 33.8 of sodium were used in this experiment. When the sodium had disappeared a solution of 55 grams of thiourea in 400 cc. of water was prepared (38 grams is one-half the calculated amount). Lumps of ice were added to the solution of the salt and the ether solution. The whole was shaken and allowed to stand overnight. The deep red solution was concentrated on the steam bath and finally cooled and acetic acid added. The precipitate weighed 27 grams, and from the filtrate 3 grams more were obtained on standing.

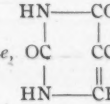
XIX. One hundred grams of each ester were condensed with 2 grams more than the calculated amount of sodium.

The whole was mixed with a saturated solution of 70 grams of thiourea in ice water. After standing a few minutes it was warmed and acetic acid added. Fifteen grams of 2-thiothymine were obtained.

The following table gives the results of the condensation of ethyl sodiumformylpropionate with thiourea in aqueous solution.

	Weight of propionic ester.	Weight of ethyl sodium-formyl-propionate.	Weight of 2-thio-thymine obtained.	Calculated weight of 2-thio-thymine from 100 grams ester.	Per cent. yield of 2-thio-thymine.	Calculated weight of thymine from 100 grams ester.
XVI	...	17[1]	2.5	17.4	12.5	15.4
XVII	100	120[1]	14.5	14.5	10.4	12.8
XVIII	150	180[1]	30.0	20.0	14.4	17.7
XIX	100	120[1]	15.0	15.0	10.7	13.3

The average yield of thymine by this method is 14.8 grams from 100 grams of ethyl propionate. This is only 11.9 per cent. of the calculated.

The Preparation of Thymine,  .—It was shown by Wheeler and Merriam that 2-methylmercapto-5-methyl-6-oxypyrimidine[2] gave 99 per cent. of the calculated amount of thymine when boiled with hydrochloric acid. The ethylmercapto derivative gives a similar result.

2-Thiothymine, like 2-thiouracil, is easily desulphurized by simply evaporating its aqueous solution with chloracetic acid.[3] For example, 3 grams of 2-thiothymine were dissolved in 250 cc. of boiling water and 3 grams of chloracetic acid were added. The solution was then evaporated to dryness on the steam bath and the residue was washed with 15–20 cc. of alcohol. It was free from sulphur and weighed 2.55 grams or 95.8 per cent. of the calculated. On evaporating the alcoholic washings more was obtained. The washed ma-

[1] Calculated from average yield of salt.
[2] This Journal, **29**, 487 (1903).
[3] *Ibid.*, **40**, 552 (1908).

terial consisted of snow-white crystals or scales and it melted at 340°. This is a higher melting point than that observed for thymine from other sources. Fischer and Roeder[1] give 321°, Wheeler and Merriam[2] 326°. A nitrogen determination by W. F. Storey gave:

	Calculated for $C_5H_6O_2N_2$.	Found.
N	22.22	22.21

In desulphurizing larger quantities it is unnecessary to dissolve all the material at first and relatively less chloracetic acid may be used.

Properties of 2-Thiothymine.—The properties of 2-thiothymine and its salts have been investigated by W. F. Storey. When the substance is first obtained by acidifying the alkaline solutions with acetic acid it separates slowly, usually not all at once, as a crystalline brownish-white precipitate. It has about the same solubility in water as in alcohol and it crystallizes from these solvents in fairly stout prisms, which have a tendency to retain the color of the solutions. One hundred parts of water at 20° dissolved 0.133 part of 2-thiothymine. This is the average of two closely agreeing determinations. Thymine is more than twice as soluble in water. Mr. Storey found that 100 parts of water at 23° dissolved 0.303 part thymine.

	Calculated for $C_5H_6ON_2S$.	Found.
N	19.71	19.67

2-Thiothymine has more pronounced acid properties than thymine. When crystallized from aqueous ammonia it retains ammonia. On drying, the amount of ammonia retained (21.86 per cent. nitrogen) was less than that calculated for a 1 : 1 salt (26.41 per cent. nitrogen). The salts of the alkali metals are very soluble in water. A solution of the sodium salt gave with silver nitrate an amorphous white precipitate, which did not blacken on boiling. The boiling

[1] Ber. d. chem. Ges., **34**, 3751 (1901).
[2] *Loc. cit.*

aqueous solution gives a white precipitate with mercuric chloride. It did not blacken on boiling alone or in the presence of alkali.

The sodium salt of 2-thiothymine, $C_5H_5ON_2SNa.1.5H_2O$, appears to be less soluble than the potassium salt. It was formed by dissolving the pyrimidine in water containing the calculated quantity of sodium hydroxide, concentrating and then crystallizing from aqueous alcohol. It formed radiating prisms which did not melt at 300°.

	Calculated for $C_5H_5ON_2SNa.1.5H_2O$.	Found.	
N	14.73	14.73	14.58
H_2O	14.21	14.65	...

The potassium salt, $C_5H_5ON_2SK.H_2O$, is soluble in less than three parts of water. From dilute alcohol it forms radiating, colorless prisms, similar to the sodium salt.

	Calculated for $C_5H_5ON_2SK.H_2O$.	Found.
N	14.14	13.83

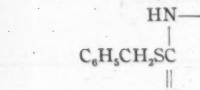
The Copper Salt, $C_5H_4ON_2SCu.H_2O$.—This salt was prepared by adding copper sulphate in aqueous solution to a hot saturated aqueous solution of 2-thiothymine. It formed a green, amorphous precipitate, which was washed with water and dried over sulphuric acid.

	Calculated for $C_5H_4ON_2SCu.H_2O$.	Found.
N	12.58	12.52
H_2O	8.08	7.79

It may be mentioned that the corresponding copper salt of 2-thiouracil, which also contains one molecule of water,[1] has a mustard-yellow color. These salts do not blacken on boiling. List[2] found that 2-thio-4-methyluracil in hot, saturated, aqueous solution gave a yellow precipitate with copper sulphate (this salt was anhydrous), while if the potassium salt was used a green copper salt was obtained.

[1] Wheeler and Liddle: *Loc. cit.*
[2] Ann. Chem. (Liebig), **236**, 9, 11 (1886).

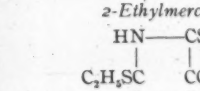
2-Benzylmercapto-5-methyl-6-oxypyrimidine,



from the above potassium salt by warming in alcoholic solution with benzyl chloride. From dilute alcohol it formed colorless needles, which melted to a clear oil at 204°–205°.

	Calculated for $C_{12}H_{12}ON_2S$.	Found.
N	12.07	12.25

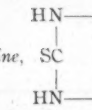
2-Ethylmercapto-5-methyl-6-thiopyrimidine,



.—An alcoholic solution of potassium hydrosulphide was prepared by saturating a solution of 57 grams of potassium hydroxide in 250 cc. of alcohol with hydrogen sulphide. To this solution 24 grams of 2-ethylmercapto-5-methyl-6-chlorpyrimidine[1] were added. The reaction began immediately and after warming on the steam bath for nearly an hour the solution was evaporated to dryness. The residue dissolved completely in water and on acidifying with acetic acid a bulky precipitate separated. After washing with water and drying it was found that the yield was practically quantitative. The crude material melted at about 175° to a clear oil and on further heating it solidified at 180°–190° and remained solid until 280° was reached, when it melted with some effervescence. The substance dissolved easily in boiling alcohol. When the solution was quickly cooled the material crystallized in plates, but when allowed to cool slowly, prismatic needles separated. It then melted at 181° to a clear oil; the pure material, on further heating, did not solidify.

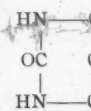
	Calculated for $C_7H_{10}N_2S_2$.	Found.
N	15.05	14.91

[1] Wheeler and Johnson: THIS JOURNAL, **31**, 595 (1904).



2,6-Dithiothymine, $C_5H_6N_2S_2$.—Two grams of 2-ethyl-mercapto-5-methyl-6-thiopyrimidine were heated in an oil bath at 215°. The substance melted and a small portion sublimed. On passing perfectly dry hydrogen chloride into the molten mass the material almost immediately solidified. The passage of the gas was continued for about five minutes. After cooling, the solid was treated with ammonium hydroxide, which dissolved the greater part, leaving a small amount of a pungent smelling oil. This was separated from the ammonia solution and the latter was acidified with acetic acid. A bulky yellow precipitate resulted, which was only slightly soluble in water but dissolved fairly easily in alcohol, and then, on cooling, gave bunches of small, bright yellow needles. They melted at 281° with decomposition and effervescence.

	Calculated for $C_5H_6N_2S_2$.	Found.
N	17.94	18.14



6-Thiothymine, $C_5H_6N_2OS$.—When 2-ethylmercapto-5-methyl-6-thiopyrimidine is heated with strong hydrochloric acid it does not smoothly go into 6-thiothymine as might be expected from analogy with the corresponding 4-methyl compound, but instead it shows a strong tendency to lose sulphur from the 6-position and pass directly into thymine. In fact, by boiling ten grams of the 2-ethylmercapto-6-thiopyrimidine for one and a half hours with strong hydrochloric acid and then twice evaporating to dryness with additional acid, very pure thymine was obtained which, after one recrystallization, gave no test for sulphur and melted at 340°. A nitrogen determination gave 22.22 per cent. nitrogen. This is the calculated value for thymine.

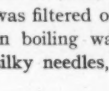
By a less vigorous treatment with acid, the decomposition

was not carried so far and a small yield of 6-thiothymine was obtained. Several experiments were required to show the conditions best adapted to obtaining this result. It was found advisable to stop the hydrolysis while there still remained some unchanged mercapto derivative. This was then extracted by means of alcohol, leaving a mixture of 6-thiothymine with a small amount of thymine. These were separated by crystallizing from water.

Nine grams of 2-ethylmercapto-5-methyl-6-thiopyrimidine were twice evaporated to dryness on the steam bath with 45 cc. of concentrated hydrochloric acid and an equal quantity of water. The dry residue was boiled for a few minutes with 100 cc. of alcohol and the portion which remained undissolved was filtered off. This weighed 4.2 grams. It was dissolved in boiling water and on cooling gave bright yellow, matted, silky needles, which melted with some effervescence at 330°.

	Calculated for $C_5H_6ON_2S$.	Found.
N	19.72	19.98

2-Oxy-5-methyl-6-methylmercaptopyrimidine,



.—Four grams of 6-thiothymine were dissolved with 1.58 grams of potassium hydroxide in 125 cc. of alcohol and 20 cc. of water. The change from the yellow pyrimidine to the potassium salt was marked by an immediate change to a white color. Four grams of methyl iodide were added to the solution and the mixture was warmed for 15 minutes on the water bath and then allowed to stand overnight. The reaction was complete at the end of this time and the solution became neutral. The alcohol was evaporated and the residue was found to be easily soluble in hot water. On crystallizing from this solvent bunches of light yellow, prismatic needles were obtained which, after two recrystallizations from alcohol, melted at 205°–211°.

	Calculated for $C_6H_8ON_2S$.	Found. I.	Found. II.
N	17.94	18.08	18.14

2-Oxy-3,5-dimethyl-6-methylmercaptopyrimidine,

—Four and seven-tenths grams of potassium hydroxide and 4.4 grams of 2-oxy-5-methyl-6-methylmercaptopyrimidine were dissolved in 150 cc. of 95 per cent. alcohol. Twelve grams of methyl iodide, or three molecular quantities, were added and the mixture was warmed for an hour on the steam bath under a return condenser. The solution then became neutral. After evaporating off the alcohol, the solid residue was extracted three times with boiling chloroform. An oily residue separated from the chloroform solution which solidified to a white solid on being stirred. It weighed 4.5 grams, or 94 per cent. of the theoretical amount of dimethylmethylmercaptopyrimidine. This material was extremely soluble in alcohol. It also dissolved easily in boiling water and benzene. From benzene solutions it crystallized in clusters of crystals resembling grains of wheat. From the water solutions, which had a marked tendency to remain supersaturated even after standing several hours, the substance crystallized in white, prismatic needles, which melted to a colorless oil at 83°.

	Calculated for $C_7H_{10}ON_2S$.	Found.
N	16.4	16.6

Treatment with Hydrochloric Acid: 3-Methylthymine.—In order to determine the structure of the above compoud two grams of it were boiled for 3 hours with 25 cc. of concentrated hydrochloric acid and an equal quantity of water, under a return condenser. On evaporating off the acid 1.4 grams of a white solid was left behind, which melted at 281°–283°. One crystallization of this from water gave one gram of material melting at 284° and exhibiting all the properties of 3-methylthymine, as described by Johnson and Clapp.[1] Especially noticeable were the two forms of crystals (needles and prisms)

[1] J. Biol. Chem., **5**, 49 (1908).

described. When this sample was mixed with a sample of their material the melting point was unchanged.

	Calculated for $C_6H_9O_2N_3$.	Found.
N	20.0	20.1

The mother liquor from this compound was carefully examined for the isomeric 1-methylthymine, but this substance was not found.

In order to determine whether or not any of the isomeric 2-oxy-1,5-dimethyl-6-methylmercaptopyrimidine had been formed with the 3,5-dimethyl derivative, the mother liquors from the crystallization of 2-oxy-3,5-dimethyl-6-methylmercaptopyrimidine were boiled for 3 hours with hydrochloric acid, under a return condenser. After evaporating the acid the solid residue weighed 1.1 grams. From this, by crystallizing from water, were recovered 0.8 gram of nearly pure 3-methylthymine, melting at 275°–281° and showing the characteristic properties. There was also obtained a very small quantity (0.15 gram) of another substance which sublimed in white needles. This substance melted at 153°–155° and was extremely soluble in water and alcohol. Not enough was obtained for analysis, but it is probable that it was 1,3-dimethylthymine, described by Johnson and Clapp. They give the melting point as 153°. When our material was mixed with theirs the melting point was not lowered. The formation of 1,3-dimethylthymine may be explained by supposing a small amount of thymine to have been left in the 6-thiothymine. The difficulty of obtaining 6-thiothymine free from thymine has been noted above. Thymine, on methylation, would give 1,3-dimethylthymine.

No evidence could be found here of the presence of 1-methylthymine. It seems fair to conclude, therefore, that under the conditions employed in the methylation of this 6-methylmercaptopyrimidine only a 3-derivative was formed.

New Haven, Conn.,
September, 1909.

THE ABSORPTION SPECTRA OF VARIOUS SALTS IN SOLUTION, AND THE EFFECT OF TEMPERATURE ON SUCH SPECTRA.

[TWENTY-SIXTH COMMUNICATION.]

By Harry C. Jones and W. W. Strong.

(A report on part of the work on absorption spectra that is being carried on with the aid of a Grant from the Carnegie Institution of Washington.)

PART I.—THE ABSORPTION SPECTRA OF VARIOUS POTASSIUM, URANIUM AND NEODYMIUM COMPOUNDS.

Outline.—I. Experimental Methods and Preparation of Solutions. II. Absorption Spectra of Potassium Salts in Aqueous Solutions. III. The Absorption Spectra of Uranium Compounds. IV. The Absorption Spectrum of Uranyl Chloride: (*a*) in Water, (*b*) as Affected by Calcium and Aluminium Chlorides, (*c*) in Methyl Alcohol, (*d*) as an Anhydrous Salt, (*e*) in Methyl Alcohol and Water, (*f*) in Ethyl Alcohol, (g) with Calcium Chloride in Methyl Alcohol. V. The Absorption Spectrum of Uranyl Nitrate: (*a*) in Water, (*b*) as a Crystalline Salt, (*c*) as Affected by Dilution, (*d*) in Methyl Alcohol, (*e*) in Mixtures of Methyl Alcohol and Water, (*f*) in Ethyl Alcohol, (g) as an Anhydrous Salt. VI. The Absorption Spectra of Uranyl Bromide, Sulphate and Acetate: (*a*) Uranyl Bromide in Water, (*b*) Uranyl Sulphate in Water, (*c*) Uranyl Acetate in Water, (*d*) the Anhydrous Acetate, (*e*) Uranyl Acetate in Methyl Alcohol, (*f*) the Bands of the Acetate. VII. The Phosphorescence and Fluorescence of Uranium Compounds. VIII. The Absorption Spectrum of Uranous Salts. IX. The Various Uranium Spectra. X. The Absorption Spectra of Neodymium Salts: (*a*) in Glycerol. XI. Summary.

Description of Plates.

Plate I. Uranyl Chloride in Methyl Alcohol.—A. Beer's Law. B. Depth Cell Constant, 6 mm.

Plate II. Uranyl and Calcium Chlorides in Methyl Alcohol. Depth Cell Constant.—A. 6 mm. B. 3 mm.

Plate III. Uranyl Nitrate, Sulphate and Acetate.

Plate IV. A. Uranyl Nitrate. B. Uranous Chloride.

Plate V. Uranyl Bromide in Water.—A. Beer's Law. B. Depth Cell Constant.

Plate VI. Uranyl Acetate in Water.—A. Beer's Law. B. Depth Cell Constant.

Plate VII. A. Uranous Sulphate. B. Uranous Chloride.

Plate VIII. Uranous Chloride.—A. In Water. B. In Methyl Alcohol.

I. Experimental Methods.

On account of the large number of bands in the absorption spectra of uranium and the rare earth salts, a study of these spectra is more interesting and more fruitful of results than the study of the spectra of the ordinary colored salts like those of nickel or copper. The absorption spectra of the ferricyanide, ferrocyanide, chromate and dichromate of potassium, the acetate, bromide, chloride, nitrate and sulphate of uranyl in water, the acetate, nitrate and chloride of uranyl in methyl alcohol, and the nitrate and chloride of uranyl in ethyl alcohol have been mapped, and Beer's law, as well as the effect of foreign substances on the absorption spectra, have been tested for these salts. The absorption spectra of two uranous salts, the chloride and sulphate, have been photographed and those of neodymium chloride in pure glycerol and in mixtures of glycerol and water have been studied. In this work the methods used by Jones and Uhler[1] and Jones and Anderson[2] have in the main been employed.

The investigations of the effect of changes in temperature on the absorption spectra of solutions have been confined to different concentration of aqueous solutions of the chloride, nitrate, acetate, sulphate and sulphocyanate of cobalt, the chloride, acetate and sulphate of nickel, the chloride, sulphate and acetate of chromium, chrome alum, the nitrate and bromide of copper, uranous chloride, erbium chloride, the chloride and nitrate of praseodymium, the sulphate, acetate, chloride and nitrate of uranyl, and the chloride, bromide and nitrate of neodymium. Spectrograms of the absorption spectra for a given concentration of a salt, with a constant thickness of layer, have been made for every 15° between 0° and 90° C.

To make a spectrogram, light from a Nernst glower and from a spark is allowed to pass through the solution that is being investigated. It is then focused upon the slit of a spectroscope, and, falling then on a concave grating, is spread out into a spectrum on the film upon which it is photographed. The films used were made by Wratten and Wainwright, of

[1] Carnegie Institution of Washington, Publication No. 60.
[2] *Ibid.*, No. 110.

Croyden, England, and were very uniformly sensitive to light from λ 2100 to λ 7200.

The sectional diagram (Fig. I) will make the experimental arrangement of the apparatus clearer. N is a Nernst glower which is arranged to slide along the rod AB. P and P' are quartz prisms which are held by a lid L. The prism P is

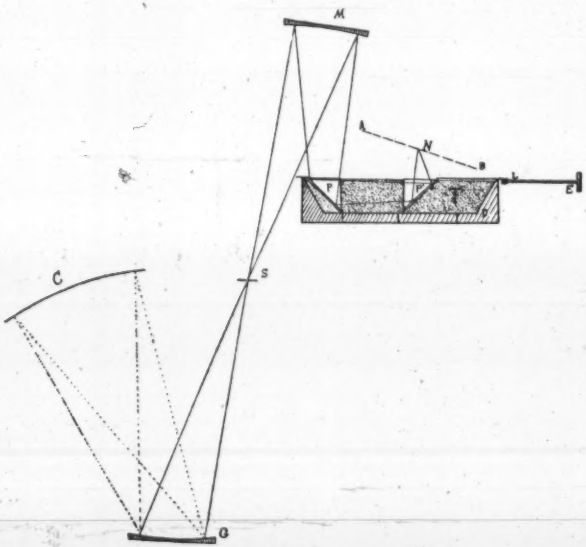


Fig. I.

stationary, whereas the prism P' can be moved by the traveling carriage E back and forth through the trough T, which contains the solution whose absorption spectrum is being investigated. AB is so inclined that the optical length of the light beam from N to P', P and the concave mirror M shall be constant, whatever the length of the solution between P and P' may be. The greatest length of path PP' used was

200 mm. The hypothenuse faces of P and P' are backed by air films which are enclosed by glass plates cemented to the quartz prisms

Considerable difficulty was experienced in finding a cement that would adhere to the polished quartz prisms at the higher temperatures. For aqueous solutions baked caoutchouc was found to work fairly well. D is a brass box holding the trough T. D is filled with oil and is placed in a water bath whose temperature can be varied between 0° and 90° C. The path of the beam of light is then from the Nernst glower (N) or spark to the quartz prism P'. The light is totally reflected from the hypothenuse face of this prism through the solution to P. This prism also has its hypothenuse face backed by an air-film, so that the light is totally reflected upwards to the concave speculum mirror at M. M focuses the light on the slit of the Rowland concave grating spectroscope, G being the grating and C the focal curve of the spectrum. The prism arrangement was designed by Dr. John A. Anderson.

This apparatus was found to work very well for aqueous solutions. Some evaporation took place at the higher temperatures, but distilled water was added in proper quantity and mixed with the solution so as to keep the concentration constant. By using troughs of different lengths it was possible to vary the length of salt solution through which the light beam passed from 1 to 200 mm. One inconvenience was experienced at low temperatures; moisture would sometimes condense upon the exposed prism faces. To overcome this an air blast was directed upon these faces and this helped very materially to prevent the condensation of moisture.

For the investigation of glycerol and other solutions a cell made of fused silica was used. The cell, as received from the Silica Syndicate Company, did not have plane parallel ends. At the suggestion of Dr. Pfund these were ground down with finely powdered emery and rouge. In this way a very serviceable cell was obtained.

For work on the effect of high temperatures on absorption spectra, a closed iron cell is being made. This is intended to stand the pressures exerted by the alcohols, acetone, ether,

water, etc., at their critical temperatures. The ends will contain quartz windows and the whole interior of the cell will be lined with gold. At the same time a radiomicrometer is being made and an apparatus is being devised by means of which quantitative measurements of the energy absorption for all parts of the spectrum can be obtained. A fuller description of the apparatus will be given later.

In the case of solids, the time of exposure is necessarily long, usually occupying several hours. It is very necessary in this case to screen off stray light. The method is very simple—consisting in focusing by means of mirrors or lenses the light from a Nernst glower or an arc upon the salt. The salt is placed a short distance from the slit of the spectroscope so that the directly reflected light does not enter the slit. By this means only the diffusely reflected light enters the slit and in general this light has penetrated somewhat into the salt and, accordingly, some wave lengths are partly or wholly absorbed. The salt is placed at such a distance that the grating is completely filled with the beam of diffusely reflected light entering the slit. This method has been used by several investigators, notably by Anderson[1] and Schultz.[2]

The observations on the phosphorescence of uranium compounds were made with the Hilger spectroscope, from which wave lengths can be read directly. Either sunlight or the light from a spark was used as the source of light by means of which the phosphorescence could be excited. Screens of variously colored glasses were used in order to find whether the wave length of the exciting light had any effect upon the phosphorescent spectrum. Especially valuable was a glass screen[3] that absorbed all wave lengths except the red, blue and violet. When this was used, no yellow or green light fell upon the phosphorescing uranium salt, so that any light in the yellow and green was necessarily due to phosphorescence

[1] Astrophysical J., **26**, No. 2, Sept., 1907.

[2] Diss., Johns Hopkins University, June, 1908.

[3] This glass screen is very useful for observing Haidinger's brushes. These brushes as seen by the naked eye are yellow and purple. Using a blue glass screen the yellow fringes become dark and show no color. With the above mentioned screen the brushes are red. These facts corroborate the theory given by G. G. Stokes: Collected Papers, **2**, p. 362.

and not to reflection. A Fuess monochromatic illuminator was also used, sunlight or arc light being focused upon the slit of the illuminator. The salt was placed in the beam of transmitted light. Usually the region of spectrum used was 50 or 100 A. U. wide. The phosphorescent light was viewed with the Hilger spectroscope.

In the work on the Zeeman effect, the large electromagnet described by Reese[1] was used. This electromagnet has very large pole pieces. A cell to hold the solution was made of thin cover-glass plates about $1.2 \times 1.2 \times 0.3$ cm. in size. The light from an arc or a Nernst glower was focused upon the solution by means of lenses, and the emergent beam of light focussed upon the slit of the spectroscope.

The concave grating described above was used for mapping the absorption spectra of solutions. A plane Rowland grating was also used for visual work, in the second and third orders of the spectrum. For polarizing the incident light Nicol prisms were used.

When anhydrous salts were employed they were dried in every case by the best methods available. Thus, chlorides were dried in a current of hydrochloric acid, bromides in a current of hydrobromic acid gas, and so on.

The usual precautions were taken in working with non-aqueous solvents to keep out all traces of moisture. Dehydrated salts were, of course, protected from contact with the air.

II. Absorption Spectra of Potassium Salts in Aqueous Solutions.

Most potassium salts in solution are colorless, and for this reason it is considered that the potassium atoms do not themselves absorb any light in the visible portion of the spectrum. Several colored potassium salts are known and the color of these are due in some way to the other atoms in the salt molecules. In the present work the absorption spectra of potassium ferricyanide, potassium ferrocyanide, potassium chromate and potassium dichromate have been studied.

Using a 3 mm. length of solution of potassium ferricyanide

[1] Astrophysical J., **12**, No. 2, Sept., 1900.

in water we find that for a normal concentration there is complete absorption of all the shorter wave lengths of light beyond λ 4800. As the concentration is decreased the edge of transmission moves continually towards the violet. It should be noticed that the region between complete absorption and complete transmission for the more concentrated solutions is quite narrow, being less than 40 Angström units, solutions of this salt being thus quite good screens for absorbing light. Continually decreasing the concentration we reach a 0.0156 normal solution, when a transmission band begins to appear. For a certain range of concentration there appears an absorption band in the region λ 4200. Further decrease in concentration results in increasing transmission throughout the violet and ultraviolet. For dilutions greater than 0.00195 normal there is almost complete transmission throughout the ultraviolet. Very faint bands appear in the regions $\lambda\lambda$ 2500 to 2600, $\lambda\lambda$ 2950 to 3050 and $\lambda\lambda$ 3200 to 3250.

Several spectrograms were made of solutions for which the product of concentration and depth of layer were kept constant. In this case the spectrograms will be identical if Beer's law holds. According to this method of testing, Beer's law was found to hold within the ranges of concentration over which the spectrum was mapped.

The absorption of aqueous solutions of potassium ferrocyanide was investigated in the same way. A half-normal solution 3 mm. deep shows that all light of shorter wave length than λ 3950 is absorbed. Keeping the depth of layer the same, it is found that with decrease in concentration the transmission gradually moves towards the ultraviolet, and for dilutions greater than 0.0078 normal there is transmission throughout the whole spectrum. Beer's law was found to hold.

A 2 normal aqueous solution of potassium chromate 3 mm. in thickness shows complete transmission of wave lengths greater than λ 4950. Decreasing the concentration causes the transmission to move gradually towards the violet, and for a 0.01 normal solution a transmission band appears at λ 3100, or, in other words, there appears an absorption band whose center is about λ 3700. As the concentration decreases

this absorption band fills up, the violet edge of the transmission band gradually pushes out into the ultraviolet, and for dilutions greater than 0.0005 normal there is complete transmission throughout the spectrum. Beer's law was found to hold for potassium chromate throughout the above ranges of concentration, except in the more concentrated solutions between 2 normal and 0.25 normal.

Potassium dichromate in water was found to have a much greater absorbing power than the solutions previously described. A one-third normal solution absorbed all wave lengths shorter than λ 5350. As the concentration is decreased the transmission extends farther and farther out into the violet. For a 0.0026 normal concentration a transmission band appears in the violet, thus giving an absorption band whose center is about λ 3800. As the concentration is further decreased transmission becomes greater and greater in the violet and ultraviolet, and is practically complete for a 0.0006 normal concentration. Beer's law has been tested between the above ranges of concentration and has been found to hold.

In photometric measurements to test Beer's law, the equation defining the quantities to be measured is

$$J = J_0 \, 10^{-Acl},$$

where J_0 is the intensity of the light that enters the solution (neglecting any loss due to reflection), J the intensity of the light as it leaves the solution, c the concentration in gram molecules of the salt per liter of solution, l the thickness of layer and A a constant if Beer's law holds. Strictly speaking, the above equation holds for monochromatic light. For ordinary white light one would have to integrate this equation over the range of wave lengths used. The equation would then have the form

$$J = J_0 \int_{\lambda_1}^{\lambda_2} e^{\beta l c} d\lambda.$$

The quantity β is called the index of absorption and A the molecular extinction coefficient. If the absorption is proportionately greater in the more concentrated solutions, then

Beer's law fails and A decreases inversely as the concentration.

From photometric measurements Settegast[1] and Sabatier[2] conclude that the absorption spectrum of potassium dichromate is the same as that of chromic acid, and that the absorption spectrum of potassium chromate is entirely different. This is corroborated by the present work. Settegast finds that Beer's law does not hold for potassium chromate and potassium dichromate, the coefficient A decreasing with increasing concentration. Grünbaum[3] finds the following values of A and ε where $\varepsilon = c/A$:

	Potassium dichromate.	
λ.	Value of A. $c = 0.034$.	Value of A. $c = 0.0034$.
509	62.4	58.0
521	28.7	26.2
536	7.24	6.2

It will be seen that the deviation here from Beer's law is in the opposite direction from that found by Settegast. Grünbaum finds that ε and therefore A depends on the depth of layer.

An example will be given where the same concentration and different depths of the solution were used:

	Value of ε for $c = 0.0034$.		
λ.	25 cm. layer.	12 cm. layer.	5 cm. layer.
521	0.0758	0.0818	0.0884
521	0.0761	0.0830	0.0897

Our work indicates that Beer's law holds for all small concentrations, and usually the deviations for concentrated solutions are very small. Of the potassium salts above described, only potassium chromate between 2 normal and 0.25 normal showed any considerable deviation from Beer's law, and in this case the absorption of the concentrated solution was greater by about 40 Angström units than would be expected if Beer's law held.

[1] Wied. Ann., **7**, 242–271 (1879).
[2] Compt. Rend., **103**, 49–52 (1886).
[3] Ann. Phys., **12**, 1004, 1011 (1903).

The present method is a very good qualitative test of Beer's law, and gives the results for each wave length, whereas most photometric methods only give integrated results over a more or less wide region of wave lengths.

III. The Absorption Spectra of Uranium Compounds.

There are quite a large number of spectra of the various compounds and decomposition products of the element uranium. The absorption spectra consist chiefly of the banded spectra of the uranyl and uranous compounds. Uranyl salts in solution are yellow and their absorption spectra consist of a broad band of general absorption in the ultraviolet, which extends more and more into the region of longer wave lengths as the amount of uranyl salt solution in the beam of light is increased. The edge of this absorption band as it gradually advances through the violet and into the blue shows several diffuse bands about fifty Angström units (A. U.) wide and about a hundred A. U. distant from each other. These comparatively fine bands, about twelve in number, are weak, having very diffuse edges, and can be photographed only when they lie near the edge of the general absorption band. Among those who have carried out investigations upon the absorption spectra of these compounds may be mentioned: H. Oeffinger,[1] H. Becquerel,[2] W. Boehlendorff,[3] O. Knoblauch,[4] E. Deussen,[5] Formánek,[6] Hartley,[7] Houstoun and Russel,[8] Jones and Strong,[9] and others.

In the discussion of the uranyl bands it will be found convenient to designate them by the letters *a*, *b*, *c*, *d*, etc., the band *a* being of the greatest wave length, and the wave lengths of the other bands gradually decreasing. In general it will be found that this classification is very useful and upon general observations it might be supposed that each band had

[1] Ueber die Lichtabsorption der Uransalze, Inaug. Diss., Tübingen, 1866.
[2] Ann. Chim. Phys., [6] **16**, 170–257 (1888).
[3] Inaug. Diss., Erlangen, 1890.
[4] Wied. Ann., **43**, 738–783 (1891).
[5] *Ibid.*, **66**, 1128–1148 (1898).
[6] Die qualitative Spectralanalyse anorg. Körper, Berlin, 1900.
[7] J. Chem. Soc., **83**, 221–246 (1903).
[8] P. Roy. Soc. Edinb., **29**, II, 68.
[9] Physik. Z., **10**, 499 (1909).

its origin in a particular vibration of the vibrating system. But at low temperatures these bands are found to consist of a number of much finer bands, and the absorption spectra become very complicated indeed, so that it is clear that changes which are observed at ordinary temperatures may be due to relative changes in the groups of five bands composing the larger bands, *a*, *b*, *c*, *d*, etc. For instance, shifts in the position of the bands, *a*, *b*, *c*, etc., due to relative changes in the intensity of the components, may be observed when the frequency of none of the component bands has been changed at all.

Becquerel[1] found that the position and intensity of the absorption bands of a crystal depend on the direction in which the light traversed the crystal. To study this phenomenon of absorption he cut sections of crystals in three different directions. One section was cut parallel to the optic axes that cut each other obliquely ("Axe moyen"), one section perpendicular to the bisector of the acute angle ("bissectrice aiguë") and another section perpendicular to the bisector of the obtuse angle ("bissectrice obtuse"). Crystals of uranyl nitrate belong to the orthorhombic type. Becquerel measured the wave lengths of the three bands, *a*, *b*, *c*, for the different sections.

Uranyl Nitrate.

	a.	*b.*	*c.*
Bissectrice aiguë	λ 4870 to λ 4840	λ 4725 to λ 4666	λ 4568 to λ 4525
Axe moyen	.....	λ 4698 to λ 4660	λ 4555 to λ 4520
Bissectrice obtuse	λ 4864	λ 4695	λ 4551

The wave lengths of the absorption bands of crystals of the double chloride of uranyl and potassium were as follows:

Bissectrice aiguë	....	λ 5007	λ 4957	λ 4905
Axe moyen	....	λ 5000	λ 4935 to 4920	....
Bissectrice obtuse	λ 5047	λ 5000	λ 4953 to 4910	....

Bissectrice aiguë	....	λ 4843	λ 4783	λ 4741	....
Axe moyen	λ 4869	....	....	λ 4741	λ 4702
Bissectrice obtuse	λ 4869	λ 4826	λ 4783	λ 4741	λ 4702

[1] *Loc. cit.*

Knoblauch[1] investigated the effect of change of concentration on the absorption spectra of various uranyl salts. He kept the amount of salt in the path of the beam of light constant but varied the concentration between wide limits. In the case of uranyl nitrate, $UO_2(NO_3)_2.6H_2O$, he compared the absorption of solutions having concentrations about 1.1 normal (c_1) and 0.0033 normal (c_2) ($c_1 : c_2 = 3428 : 1$). If the molecules of uranyl nitrate had acted like the molecules of a gas the concentrated solution would have exerted a pressure of 25.4 atmospheres and the dilute solution $^1/_{138}$ atmosphere. For both solutions the *a* (λ 4920–4850) and the *b* (λ 4780–4680) bands appeared in the same position. With uranyl acetate, $UO_2(C_2H_3O_2)_2 2H_2O$, a change in concentration of $c_1 : c_2 = 446 : 1$ did not cause any shift in the *a* (λ 4940–4870) or the *b* (λ 4820–4730) bands. The position of the edge of the ultraviolet absorption was the same for both concentrations. The absorption bands were found to be more intense for the dilute solution. Uranyl chloride in concentrations $c_1 : c_2 = 2500 : 1$ showed three absorption bands *a* (λ 4950–4870), *b* (λ 4820–4720) and *c* (λ 4650–4560). The bands were unaffected by dilution.

Knoblauch considers that deviations from Beer's law must be due to (1) a change in the molecular complex that constitutes the absorber; (2) a chemical change such as hydrolysis or hydration; (3) dissociation; (4) mutual actions which exist between the dissolved molecules in concentrated solutions that do not occur in very dilute solutions. The experimental results which he obtains for uranyl and eosin salts indicate that deviations from Beer's law cannot be explained as being due to dissociation.

Deussen[2] has made a very complete examination of the absorption spectra of various uranyl salts in different solvents and in mixtures of different solvents. Below are the wave lengths measured by Deussen:

[1] *Loc. cit.*
[2] *Ibid.*

Uranyl Nitrate.

Solvent.	*a.*	*b.*	*c.*	*d.*	*e.*
Water	4860	4720	4540	4380	4290
Ethyl alcohol	4845	4680	4490	4360	4240
Methyl alcohol	4850	4680	4490	4360	4295
Acetone	4845	4680	4490	4360	4240
Glycerol	4870	4735	4525	4350	4220
Amyl alcohol	4845	4680	4490	4360	4240
Acetic ester	4850	4685	4495	4365	4250
Ether	4850	4685	4495	4370	4255
	f.	*g.*	*h.*	*i.*	*j.*
Water	4150	4020	3870	3790	3690
Ethyl alcohol	4090	3990	3840	3750	3660
Methyl alcohol	4050	4000	3840	3750	3660
Acetone	4090	3990	3855	3760	3670
Glycerol	4060	3910	3820	3710	....
Amyl alcohol	4090	3990	3840	3750	3660
Acetic ester	4095	3995	3845	3755	3665
Ether	4100	4000	3850	3760	3670

The above wave lengths of the bands do not agree very well with our own measurements. For instance, the ethyl alcohol bands are found to have a greater wave length than the water bands. Deussen worked with mixtures of all the above solvents and water. He obtained some very remarkable results. For example, he finds that, as compared with a pure aqueous solution of uranyl nitrate, in the 50 per cent. ethyl alcohol solution all the uranyl bands are shifted towards the red. When the solvent contains 80 per cent. alcohol all the bands are shifted towards the violet, and for a pure alcohol solution all the uranyl bands are of shorter wave length than for a pure water solution.

Deussen obtained very interesting results for uranyl nitrate in mixtures of water and glycerol. As the percentage of glycerol increases the *c* and *d* bands broaden and finally, for a pure glycerol solution, form but a single band. At the same time all the other bands are shifted towards the red.

Uranyl Chloride.

Solvent.	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*
Water	4900	4735	4580	4410	4285	4140
Ethyl alcohol	4910	4745	4595	4425	4305	4200
Glycerol	4920	4755	4600	4510	4410	4280

Uranyl Chloride—(Continued).

Solvent.	*g.*	*h.*	*i.*	*j.*	
Water	4025	3925	3800	3710	....
Ethyl alcohol	4080	3990	3870	3750	....
Glycerol	4170	4030	3940	3810	3715

For uranyl chloride solutions in mixtures of water and glycerol, Deussen finds that the *c* band of the water solution breaks into two bands when the solvent is pure glycerol. Increasing percentages of glycerol cause an increased shift of the bands towards the red.

Uranyl Sulphate, $UO_2SO_4.3\frac{1}{2}H_2O$.

Solvent.	*a.*	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
Water	4885	4725	4560	4410	4310	4180	4060	3950
Ethyl alcohol	4890	4730	4565	4420	4320	4190	4070	3960
Glycerol	4890	4730	4570	4430	4340	4210	4090	3980

H. Becquerel[1] has made a number of observations on the absorption spectra of uranium compounds at low temperatures. He considers that the absorption and phosphorescent bands are parts of a single system. They have two bands in common. He states that any modification in the appearance of one set of bands for any compound is reproduced by a similar change in the other set of bands. In general, the bands found at the temperature of liquid air are moved towards the violet with respect to the same bands at ordinary temperatures. Uranyl nitrate, at ordinary temperatures, gives wide diffuse bands whose intensities come at about their middle. At the temperature of liquid air each group is resolved into several bands, and the most intense of these bands are towards the violet. A table of the wave lengths of these bands is given below.

Bois and Elias[2] find that the double sulphate of uranyl and potassium when cooled to —190° C. gives bands at $\lambda\lambda$ 4878, 4882, 4888 and 4905. These seem to broaden slightly when placed in a strong magnetic field. At 18° C. uranyl nitrate gave bands at λ 4675–4716, λ 4849–4880, and at —190° C. strong bands at λ 4679–4697, λ 4845–4849 and λ 4853–4857.

[1] Compt. Rend., **1885**, 1252; **1907**, 459, 671.
[2] Ann. Phys., **1908**, 299.

Crystals of Uranyl Nitrate.		*Double Sulphate of Uranyl and Potassium.*		*Double Chloride of Uranyl and Potassium.*	
Room temperature.	Liquid air.	Room temperature.	Liquid air.	Room temperature.	Liquid air.
Diffuse band			6500	6400–6360	
	6360		6270	6315	6360
	6170(s)		6185–6175		
6201–6150	6145–6127	6155 Weak	6155–6145(s)		
	6104		6039–5945	6055	6030(s)
	6050				5800
			5910(f)	5970–5975	5751(s)
	5856(s)	5890–5885	5887(s)	5920	
	5833(s)		5830	5776–5740(s)	5721(f)
	5782		5763	5702(f)	
	5707	5760	5715	5632(t)	5619(f)
	5630		5695–5674	5515–5481(s)	5555(f)
	5600		5647(s)	5447	5535
	5580(s)	5610–5560	5616(s)	5394(f)	5486(s)
	5553(s)		5591(s)	5275–5247(s)	5462(f)
	5490	5535	5886	5205	5435(t)
	5435	5515	5410	5161(f)	5400(f)
	5375		5427(t)	5116(f)	5373(f)
	5323(s)		5384(f)	5080(t)	5361(f)
	5297(s)		5365(s)	5065(t)	5315(f)
	5272		5347	5042	5295(s)
	5240		5338(s)	4995	5224(s)
	5190		5334		5202(f)
	5137		5138		5156(f)
5120–5060	5115		5124(f)		5196(f)
	5093(s)		5114(s)		5072
	5072(s)		5000		5040(s)
	5018		4932(s)		5012
4893–4855	4975		4910(s)		4990(f)
	4925				
	4900(s)				

Uranous salts are of a deep green color and have a very characteristic absorption spectrum, which consists of diffuse bands scattered throughout the spectrum. With the exception of a short description of a few of the bands by Formánek practically nothing has been done on the absorption of uranous salts either in solution or in the crystalline condition.

IV. The Absorption Spectrum of Uranyl Chloride.

The absorption spectrum of uranyl chloride (crystals having the composition $UO_2Cl_2.H_2O$ at ordinary temperatures) has been mapped for solutions in water, methyl and ethyl alcohols, in mixtures of these solvents and in solutions with aluminum and calcium chlorides and for the anhydrous salt.

(*a*) *Uranyl Chloride in Aqueous Solutions.*—The absorption spectrum of uranyl chloride in water was mapped for 1, 0.75, 0.50, 0.33, 0.25, 0.16 and 0.125 normal solutions, the depth of layer being 3 mm. and the time of exposure to the Nernst glower with a current of 0.8 ampere being 1 minute. The slit width was 0.08 mm.

The absorption spectra of the chloride and bromide are very similar, the blue-violet absorption band being slightly stronger for the chloride. The uranyl bands are very broad and diffuse for both salts, being slightly more diffuse for the chloride. Practically only the *a*, *b* and *c* bands appear with any strength.

Of these, *a* and *b* are the stronger. They appear of about the same intensity and are about 80 A. U. wide. For the bromide *a* is considerably weaker than *b*. The sulphate and nitrate, on the other hand, show practically all of the uranyl bands, the bands being the strongest in the sulphate solution. In this salt solution the *b* and *c* bands are six to ten times as strong as the *a* band. In the nitrate this difference is not so marked, and the bands appear somewhat finer than in the case of any other salt. The acetate shows the greatest absorption of all the salts mentioned above. Here, the *a*, *b* and *c* bands are very faint. About half a dozen very faint bands appear together.

For the 1 N solution the ultraviolet and blue-violet bands merge together and end at λ 4550. For the 0.75 N solution the blue-violet band is limited by regions of absorption beyond the limits $\lambda\lambda$ 4500 and 3900, for the 0.5 N solution, $\lambda\lambda$ 4470 and 3950, and for the 0.33 N solution, $\lambda\lambda$ 4400 and 4050, the center of the band thus being at λ 4200. Collecting the results of their measurements of the center of this blue-violet band we have:

Uranyl chloride	λ 4200
Uranyl nitrate	λ 4150
Uranyl bromide	λ 4250
Uranyl acetate	λ 4200
Uranyl sulphate	λ 4180

Therefore, for all these salts, the blue-violet bands appear at the same position.

The band also widens with increase of concentration quite uniformly. The edges of the ultraviolet band are: 0.75 N λ 3700, 0.5 N λ 3670, 0.33 N λ 3650, 0.25 N λ 3630, 0.16 N λ 3600, and 0.125 N λ 3570.

The positions of three of the uranyl bands (*a*, *b* and *c*) were measured. On account of the extreme faintness of *c* the result for this band is not very accurate.

a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
4920	4740	4560	4460	4315	4170	4025

In addition to the bands already given, uranyl chloride has several remarkably fine bands in the green. These bands are not more than 5 A. U. wide and were first seen on spectrograms made on the Wratten and Wainwright red-sensitive films. They appear only for aqueous solutions of uranyl chloride. The addition of calcium or aluminium chloride causes them to disappear. They do not appear in the alcoholic solutions. Uranyl sulphate shows the same bands at about the same position as the chloride but much weaker—too weak to be separa ted. The wave lengths are as follows:

$\lambda\lambda$ 5185, 5200, 6000, 6020, 6040 and 6070.

So far as the writers know, this is the first time that these bands have been noticed in aqueous solutions. Uranyl salts

give a spectrum of emission through phosphorescence, and this spectrum appears to be a continuation of the absorption spectra to longer wave lengths. Becquerel[1] has shown that any uranyl compound showing a modification of the absorption bands shows a similar modification of the emission phosphorescent bands.

A series of spectrograms was made to test Beer's law. Exposures were made under the standard conditions with 1, 0.75, 0.5, 0.33, 0.25, 0.16, 0.125 normal solutions of uranyl chloride, the corresponding depths of cell being 3, 4, 6, 9, 13, 18 and 24 mm.

There is a slight transmission band in the ultraviolet between the blue-violet and ultraviolet bands. This transmission region is roughly 100 A. U. wide, and is so faint that it does not appear upon the printed plates. This band obeys Beer's law. The long wave length edge of the blue-violet absorption band, however, deviates slightly from Beer's law. For the 1, 0.75, 0.5 and 0.33 normal solutions the absorption is slightly greater than for the 0.25 normal solution. The 0.25, 0.16 and 0.125 normal solutions obey Beer's law. The edge for the 1 normal solution is roughly 75 A. U. nearer the red than for the 0.25 normal solution. The uranyl bands *a* and *b* are slightly stronger for the more concentrated solutions. A similar run for Beer's law was made between the concentrations 0.125 and 0.0156 normal. Beer's law holds in this case, the absorption being complete for wave lengths less than λ 4150. The uranyl bands do not appear at all.

(*b*) *Uranyl, Calcium and Aluminium Chlorides in Water.*— Spectrograms were taken of aqueous solutions of uranyl chloride of a constant concentration to which varying amounts of calcium chloride were added. The addition of calcium chloride causes the ultraviolet, the blue-violet and the uranyl bands to widen generally. The effect upon the uranyl bands is, however, very small. The effect of aluminium chloride, on the other hand, is very great. The two narrow and faint bands at λ 5200 appear only in the pure aqueous

[1] Mém. Acad. Sci., **40**, 1872.

solution of uranyl chloride. The *a* band in the aqueous solution is about 60 A. U. wide, and is almost as intense as the *b* band. The addition of aluminium chloride causes the band to become quite narrow, about 25 A. U. wide. A slight addition of aluminium chloride decreases the intensity of the band very considerably. Further increases in the amount of aluminium have very little effect. The addition of aluminium chloride also causes the bands to shift to the red, the shifts in some instances amounting to 25 A. U. The intensity of the *b* and *c* bands is very greatly increased by the addition of aluminium chloride; and by making the solution about 2 normal with aluminium chloride these bands are shifted about 30 A. U. to the red as compared with the same bands for the pure uranyl chloride solution. The *d*, *e*, *f*, *g* and *h* bands are also increased in intensity, but are but very slightly shifted to the red. The *d* and *e* bands are widened so that they form practically a single band.

(*c*) *Uranyl Chloride in Methyl Alcohol.*—The first spectrogram for mapping out the absorption spectrum of uranyl chloride in methyl alcohol is given in B, Plate I. Exposures were made to the Nernst glower for 1 minute with a slit width of 0.08 mm. and a current of 0.8 ampere. The depth of cell is 6 mm. for each strip. Beginning with the strip nearest the numbered scale the concentrations are 0.0625, 0.079, 0.1, 0.125, 0.158, 0.2 and 0.25 normal.

The alcoholic solution of uranyl chloride is very similar to the alcoholic solution of uranyl nitrate, the absorbing power of both solutions being considerably greater than that of aqueous solutions. The aqueous solution of uranyl chloride shows only a few of the characteristic uranyl bands in its absorption spectrum. In the alcoholic solution, however, they appear very strongly.

Starting with the most concentrated solution, whose absorption spectrum is given by the strip furthest from the numbered scale, we have the bands *a* and *b* appearing and all wave lengths less than λ 4500 completely absorbed. The *b* band is very strong, the *a* band very weak—almost lost in this region of the spectrum where the film is less sensitive to the light.

For the next concentration, 2 N, we have a weak transmission band appearing in the ultraviolet. Other uranyl bands appear as the concentration is decreased. We shall now consider the blue-violet band. For the 0.2 N solution its limits are $\lambda\lambda$ 4450 and 3800, for the 0.158 N solution $\lambda\lambda$ 4400 and 3900, and for the 0.125 N solution $\lambda\lambda$ 4350 and 3900. The middle of the band would thus come at about λ 4100.

The uranyl bands *a*, *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i* and *j* all appear. The bands *b* and *c* are the largest and strongest. Band *a* is relatively much weaker. The appearance of the bands is somewhat like the bands of uranyl nitrate in methyl alcohol. The uranyl nitrate bands are on the whole considerably fainter and narrower than the uranyl chloride bands. Bands *a*, *b* and *c* are almost of the same intensity in the case of the nitrate, all being quite faint. The blue-violet band is much more diffuse in the spectrum of the uranyl nitrate. The following are the wave lengths of the bands of uranyl chloride, the second row giving the wave lengths of the same bands for uranyl nitrate in methyl alcohol:

	a.	*b.*	*c.*	*d.*	*e.*
Chloride	4930	4760	4610	4465	4345
Nitrate	4930	4760	4610	4460	4325
	f.	*g.*	*h.*	*i.*	*j.*
Chloride	4220	4090	3980	3860	3760
Nitrate	4190	4070	3970	3855	....

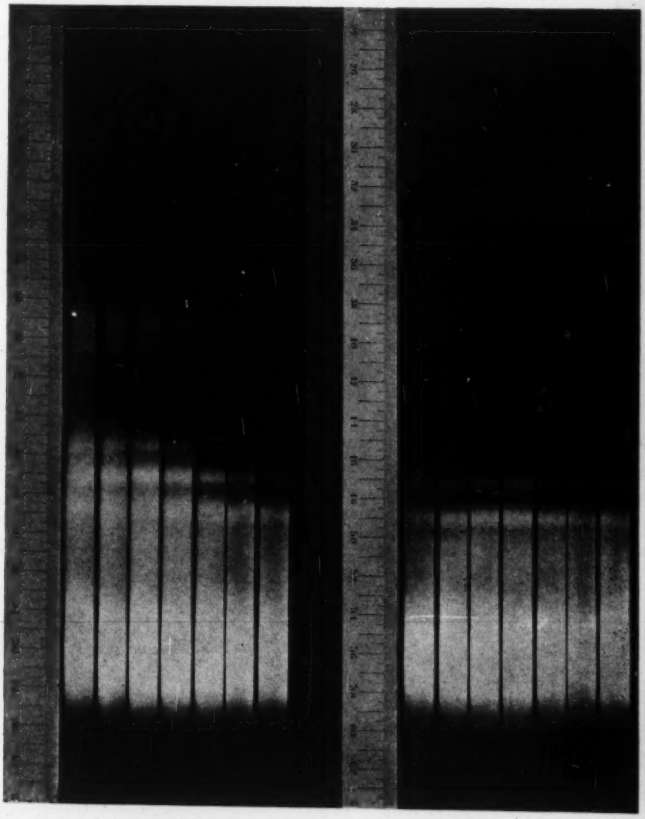
The *a*, *b* and *c* bands of the chloride and nitrate come at about the same positions, but the *e*, *f*, *g* and *h* bands of the chloride are all shifted towards the red as compared with the same bands of the nitrate. The uranyl chloride bands in water are slightly shifted towards the violet with reference to the uranyl chloride bands in methyl alcohol.

The relative intensities of the bands do not completely agree with those given by Deussen.[1] In the main, the results agree fairly well with his, he finding that in alcohol the bands are shifted towards the red.

A plate was made in exactly the same way as B, Plate I, the only difference being that the depth of cell was 15 mm.

[1] Ann. Phys., **66**, 1137 (1898).

Plate I.



B A

whereas for the spectrogram previously described the depth of cell was only 3 mm. This spectrogram shows very well how a uranyl band increases in intensity as the edge of the blue-violet band approaches it.

The *a* band thus increases in intensity and in width with increase of concentration. The band also seems to widen unsymmetrically, although the disymmetry may be due in part to the unequal sensitiveness of the photographic film to different wave lengths of light in this part of the spectrum.

The spectrogram A, Plate I, taken to test Beer's law, was made by exposures of 1 minute to the Nernst glower with a current of 0.8 ampere, and slit width of 0.08 mm. Exposures to the spark in order to get reference lines were made only in the ultraviolet. Starting with the strip next to the numbered scale, the concentrations were 0.0625, 0.079, 0.1, 0.125, 0.158, 0.2 and 0.25 normal, the corresponding depths of cell being 24, 19, 15, 12, 9.5, 7.5 and 6 mm.

Beer's law holds for the alcoholic solutions between 0.25 N and 0.06 N. The limit of absorption is at λ 4650 and is quite sharp, this being the long wave length edge of the uranyl *c* band. The *b* band is very strong, the *a* band quite weak.

A very faint transmission band appears at λ 3850 and is about 100 A. U. wide. This band also obeys Beer's law and is, in fact, quite a sensitive index for any deviations from this law.

(*d*) *Absorption Spectrum of Anhydrous Uranyl Chloride.*—The absorption spectrum of the anhydrous chloride was photographed in the same way as that of the anhydrous nitrate. The bands differ considerably from the bands of the aqueous solution, and one cannot tell very well whether they are identical with the corresponding *a*, *b*, *c*, etc., bands of the solution or not. Their wave lengths are approximately as follows: $\lambda\lambda$ 4950 (narrow), 4860, 4765, 4700, 4615, 4540, 4460, 4320, 4290, 4160, 4050 and 3940.

(*e*) *Absorption Spectrum of Uranyl Chloride in Methyl Alcohol and Water.*—A spectrogram was made of a solution of uranyl chloride of constant concentration in mixtures of methyl alcohol and water. A small addition of water causes

a considerable decrease in the absorption power of the uranyl chloride. When the amount of water has reached about 16 per cent. very little further change is produced by further increasing the amount of water. The most important effect of the addition of water is the effect upon the uranyl bands. For a pure alcoholic solution the *a* and *b* bands appear, the *b* band being quite intense. Addition of water causes both *a* and *b* to decrease in intensity and apparently to shift towards the violet. A spectrogram for a solution of smaller concentration shows the *a*, *b*, *c*, *f*, *g*, *h* and *i* bands; the solution containing 8 per cent. water the *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i* and *j* bands; the 16 per cent. water solution *b*, *c*, *d*, *e*, *f*, *g*, *h*, *i* and *j*; the 24 per cent. water solution shows all these bands greatly weakened; and in solutions containing a greater amount of water practically only the *b* and *c* bands appear, and these are very diffuse. The general effect upon the positions of the bands is quite remarkable, the *b* and *c* bands apparently being shifted to the violet with increase of water, whereas the ultraviolet bands appear to be shifted towards the red.

(*f*) *Absorption of Uranyl Chloride in Ethyl Alcohol.*—The absorption spectrum of uranyl chloride in ethyl alcohol shows the uranyl bands quite strongly, although they are less intense than for the methyl alcohol solution. A very interesting resemblance has been found for the various uranyl bands of different mixtures. The absorption spectrum of a solution of uranyl chloride in ethyl alcohol has been found to be almost the same as that of a methyl alcohol solution of uranyl chloride containing a 0.9 normal concentration of calcium chloride, or of an aqueous solution of uranyl chloride and a 2 normal concentration of aluminium chloride.

The positions of the uranyl bands for the ethyl alcohol solution are approximately:

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
λ	4900	4750	4580	4400	4400	4250	4100	3980	3860

The relation above mentioned comes out much better on comparing the spectrograms. The values of wave lengths thus far given do not bring this out very well on account of

the difficulty of making measurements. Much more work is to be carried on along this line, and the measurements above given are to be considered as more or less of a preliminary character.

(g) *Uranyl Chloride and Calcium Chloride in Methyl Alcohol.—Plate II, A and B.*—These spectrograms, showing the absorption spectra of mixtures of uranyl chloride and calcium chloride in methyl alcohol, were taken under the same conditions. Exposure was made to the Nernst glower for 1 minute with a slit width of 0.08 mm. and a current of 0.8 ampere. The ultraviolet standard lines were photographed with the uranyl solution removed from the light beam. In every case the concentration of uranyl chloride was 0.125 normal. Starting with the strip at the top of the spectrogram of both A and B the concentrations of calcium chloride were 0.0, 0.144, 0.0288, 0.432, 0.576, 0.72 and 0.9 N. In A the depth of solution was 6 mm, in B 3 mm.

The effect of calcium chloride on the absorption spectra of a methyl alcohol solution of uranyl chloride is very slight, notwithstanding the power of calcium chloride to combine with alcohol. An increased amount of calcium chloride causes the ultraviolet and blue-violet bands to widen slightly, as will be seen from both A and B. The change in the intensity of the uranyl bands is also very slight.

In the upper strip of B appear the bands *a*, *b*, *c*, *d*, *e*, *f*, *i* and *j*. Only one edge of *a* is to be seen clearly; *b* and *c* are clear and entirely separated; *d* is very diffuse and especially so on the violet side; *e* is also diffuse, but is a distinct band. *f*, *g* and *h* are distinct and entirely separated; *i* and *j* can also be noticed. When calcium chloride is added a very peculiar phenomenon takes place. The bands *d* and *e* come together and, as far as one can tell, form a single band. This causes the bands *f*, *g* and *h* to shift to the red, the other bands becoming too faint to be recognized. Measurements gave the following wave lengths for the solution of uranyl chloride in methyl alcohol itself: *b*, λ 4760; *c*, λ 4590; *d*, λ 4465; *e*, λ 4345; *f*, λ 4225; *g*, λ 4095; *h*, λ 3975; and *i*, λ 3860. Taking up the solution containing a 0.9 normal concentration of calcium

chloride we find that the *b* and *c* bands have remained at the same part of the spectrum. The *d* and *e* bands have combined into one large diffuse band whose position is approximately λ 4420. The *f*, *g* and *h* bands are now at $\lambda\lambda$ 4260, 4120 and 4010, respectively.

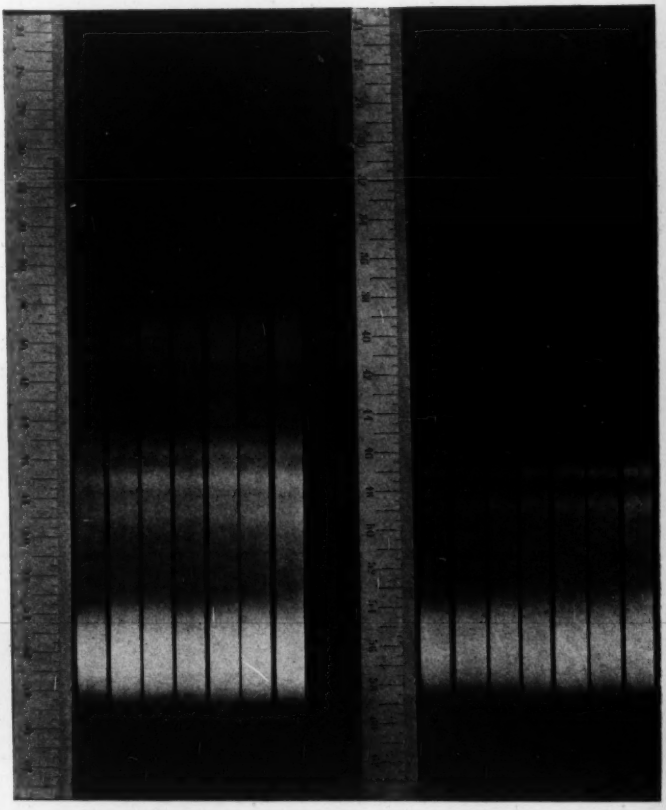
A spectrogram was also taken under conditions identical with those in A and B in every respect except that the depth of layer was made 15 mm. Here only the *a* and *b* bands appeared. The *b* band was very wide and strong, the *a* band very weak. In the pure uranyl chloride solution the *a* band was quite wide. As the amount of calcium chloride was increased the band became much narrower and its center shifted from λ 4925 for the pure uranyl chloride solution to about λ 4895 for the solution containing a 0.9 normal concentration of calcium chloride. Whether this could be accounted for as due entirely to unsymmetrical narrowing is uncertain, though it seemed that its short wave length edge was slightly shifted towards the violet.

V. Absorption Spectrum of Uranyl Nitrate under Different Conditions.

(*a*) *Uranyl Nitrate in Aqueous Solution.*—The spectrum of uranyl nitrate in water is a typical example of the uranyl salts. With a depth of solution of 3 mm. its absorption spectrum was investigated between concentrations of 1.5 normal to 0.0234 normal. For the 1.5 normal solution the absorption consists of a band in the blue-violet and absorption throughout the ultraviolet portion of the spectrum. As the concentration decreases the blue-violet band fills up with transmission, and the ultraviolet absorption is pushed farther and farther out into the ultraviolet. The blue-violet band is practically gone at a concentration of 0.5 normal, and there is almost complete transmission throughout the ultraviolet for concentrations less than 0.02 normal.

During these changes in concentration a large number of bands about 50 A. U. wide make their appearance. Near the edge of an absorption band these bands are relatively quite clear. As the absorption edge recedes from the uranyl bands,

Plate II.



B A

the general transmission is so great as to obscure them almost completely.

A, Plate IV, represents the absorption spectra of an aqueous solution of uranyl nitrate of different depths of layer. The narrow and rather weak bands shown here are the uranyl bands. Twelve of these bands have been photographed. Starting at the band of longest wave length they will be designated by the letters *a*, *b*, *c*, *d*, etc. On account of the irregularity of the distribution of light in the spark spectrum and the small intensity of the uranyl bands, the Nernst glower was used as the source of light in the ultraviolet, and long exposures were made. A screen was used that cut out all wave lengths greater than λ 4200. A represents a typical spectrogram of this kind. Starting with the spectrum strip at the top, the concentrations were 1.5, 1.1255, 0.75, 0.5, 0.375, 0.25 and 0.1875 N. The slit width was 0.08 mm. and the current through the Nernst glower 0.8 ampere. The spectra of wave lengths greater than λ 4300 represent the absorption of a depth of layer of 15 mm.; the spectra of shorter wave lengths represent the absorption of a depth of layer of 3 mm. The upper spectrum strip represents then the absorption spectrum of a 1.5 normal solution of uranyl chloride 15 mm. thick, exposure to the Nernst glower having been 1 minute. It will be seen that the uranyl band *a* comes out very strongly. The screen was then placed in the path of light and exposure of 5 minutes made to the violet and ultraviolet beyond λ 4300, a solution of uranyl nitrate of 1.5 normal concentration and 3 mm. deep being in the path of the beam of light. This amount of uranyl nitrate absorbed practically all the light in this region. A very short exposure was afterwards made to the spark in the region λ 2600, in order to get a comparison spark spectrum in this region so that the wave lengths of the uranyl bands could be measured.

Throughout this work a comparison spark spectrum usually containing the very strong line λ 2478.8 was photographed on each spectrum strip. In measuring the uranyl bands all measurements were made from this line as a standard, and although the absolute wave lengths of the uranyl bands may

not be correct to within 20 A. U., yet relatively they are probably correct to within less than 10 A. U. for the finer bands.

The second spectrum strip from the top represents in the long wave length end of the spectrum the absorption of a 15 mm. layer of a 1.125 normal solution of uranyl nitrate exposed 1 minute to the Nernst glower. The *a* band appears, although not nearly as intense as in the spectrum strip above. The region of shorter wave lengths beyond λ 4300 represents the absorption of a 3 mm. layer of a 1.125 normal solution exposed 5 minutes to the Nernst glower. A very faint transmission is shown in the region λ 3700. The ultraviolet line λ 2478.8 is shown in the comparison spark spectra. The other spectrum strips were made in a similar manner, with the concentrations given above.

By this method of exposing two new bands were detected in the ultraviolet. In aqueous solutions the intensities of the bands are much the same. In other solvents, however, and for other uranyl salts, the relative intensities of the bands change very greatly. For uranyl nitrate crystals the bands are even more closely related to each other than in aqueous solutions. The longer the wave length of the band the more intense and wide it is as a rule. The position of the long wave length bands in the orthorhombic uranyl nitrate crystals, $UO_2(NO_3)_2 6H_2O$, is the same as the position of the bands for an aqueous solution. The wave lengths of the bands are as follows:

	a.	*b.*	*c.*	*d.*	
Water sol.	4860	4720	4540	4380	Deussen.
Water sol.	4870	4705	4550	4390	Jones and Strong.
Crystals	4870	4705	4500–4565	4405	
	e.	*f.*	*g.*	*h.*	
Water sol.	4290	4150	4020	3870	Deussen.
Water sol.	....	4155	4030	3905	Jones and Strong.
Crystals	4275	4170	4050	3935	
	i.	*j.*	*k.*	*l.*	
Water sol.	3790	3690	....	....	Deussen.
Water sol.	3815	3710	3605	3515	Jones and Strong.
Crystals	3830	(3720?)	3600		

In the original film from which A, Plate I, was made all these bands except *d* could be very distinctly seen. The bands of longer wave length are slightly wider. The *i* band is considerably weaker than its neighboring bands.

(*b*) *Absorption Spectrum of Uranyl Nitrate Crystals.*—For the aqeuous solution there is no sign that the bands can be broken up. In the crystal spectrum this is not the case. The *a* band is narrow. The *b* band is also very narrow, about 15 A. U. wide. A very faint band appears about λ 4650. The *c* band, on the other hand, is very wide, about 70 A. U., and is probably double. The *d* band is about 50 A. U. wide, and the *e* band is about 70 A. U. wide and appears double. The *f* band is the most intense and is about 40 A. U. wide. The bands *g*, *h*, *i* and *j* keep decreasing in intensity respectively. The above description is of a spectrogram taken of a crystal in Canada balsam, and of course the width of the bands varies with the time of exposure and various other things. The above spectrogram showed many details, however, that other spectrograms did not. It will thus be seen that the *a*, *b*, *c*, *d*, *f* and *k* bands of the solution agree fairly well with those of the crystal, and that the crystal bands *f*, *g*, *h* and *i* are shifted towards the red with reference to the bands in the aqueous solution.

(*c*) *Effect of Dilution upon the Uranyl Bands.*—The effect of dilution on the position and intensity of the blue-violet, the ultraviolet and the uranyl bands of the acetate, nitrate and sulphate of uranyl in water was tried. The absorption spectra of solutions about 1 normal and 3 mm. deep were photographed along by the side of the absorption spectra of 0.008 normal solutions of the same salts 380 mm. deep. The absorption consisted of the blue-violet band, the ultraviolet band and the *a*, *b*, *c*, *i*, *j* and *k* bands. Between the blue-violet and ultraviolet bands there was the transmission band containing *i*, *j* and *k*. For each of the three salts this transmission band was much weaker for the dilute solution, whereas in the cases of the sulphate and nitrate the long wave length transmission edge of the blue-violet band was stronger for the more dilute solution. The opposite was true of the acetate solution. In the

dilute solution of the acetate the bands were more intense than for the more concentrated solution. There was no noticeable change in the position of the bands. Neither the intensity nor the position of the uranyl nitrate or the uranyl sulphate bands was changed by the above dilution.

A, Plate III, represents the spectrogram comparing the spectra of the same amount of uranyl salt in a concentrated and in a dilute solution. Starting with the strip adjacent to the numbered scale we have the absorption spectra of a 1.1 normal solution of uranyl nitrate in water, the depth of the cell being 3 mm. The next spectrogram is of the same solution. Then distilled water was poured into the solution until the length of column was 380 mm. The absorption spectrum of this solution is given in the third strip. The fourth strip represents the absorption of a 0.75 normal solution of uranyl sulphate, the depth of cell being 4 mm. The fifth strip is for the same solution diluted until the depth was 380 mm. The sixth strip represents the absorption of a 0.188 normal solution of uranyl acetate 14 mm. deep. The last strip is for the same solution diluted to a depth of 380 mm.

A more detailed study was made as to whether Beer's law holds for uranyl nitrate and for the other uranyl salts. The method of taking the spectrograms is the same as that used for the potassium salts.

Beer's law was found to hold for dilute solutions of uranyl nitrate in water. When the concentration is greater than 0.5 normal the absorption is greater than it should be if Beer's law held.

(*d*) *Uranyl Nitrate in Methyl Alcohol.*—In methyl alcohol the general appearance of the absorption is very similar to that of the aqueous solution, the blue-violet, the ultraviolet and uranyl bands appearing under the same general conditions as for aqueous solutions. There is a very marked deviation from Beer's law for the more concentrated solutions, however, the absorption being greater than it would be if Beer's law held. The position of the bands are quite different from the positions of the uranyl bands of the aqueous solution, or of the crystals, as shown by the following values:

Plate III.

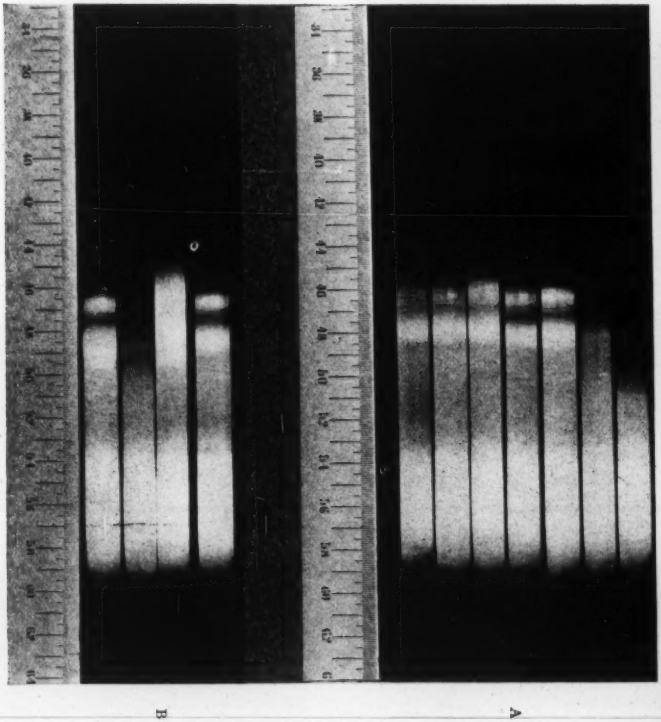
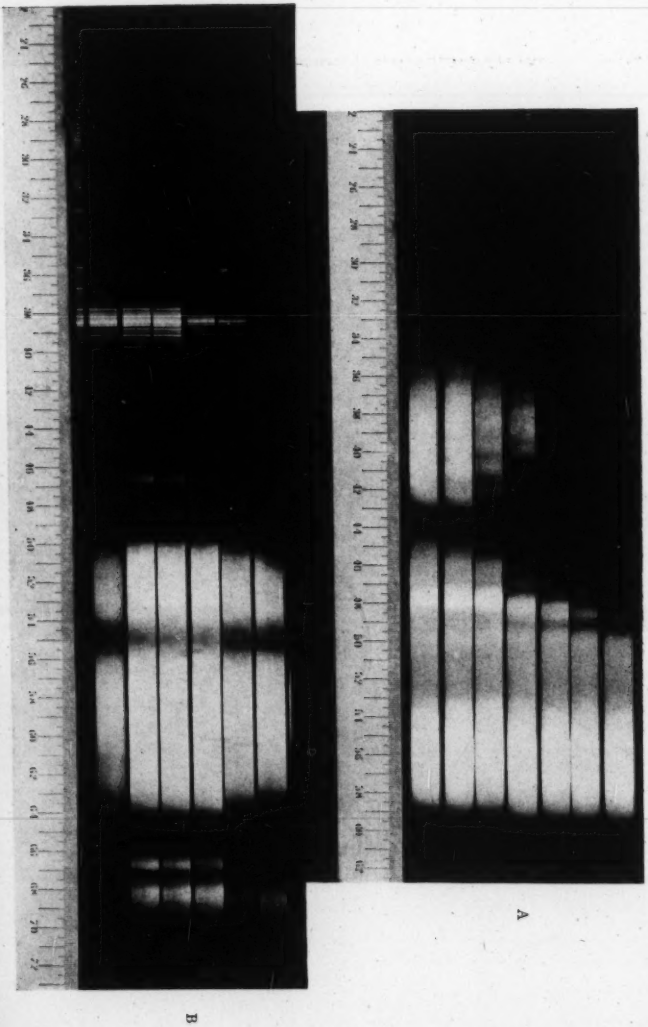


Plate IV.



B

A

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
λ	4930	4760	4610	4455	4325	4190	4070	3965	3855

(*e*) *Uranyl Nitrate in Mixtures of Methyl Alcohol and Water.*—In the previous work of Jones and Anderson[1] it was found that in some cases (for example neodymium chloride) a salt in water has a different set of absorption bands as compared with the same salt in another solvent as, *e. g.*, methyl alcohol.

When the salt is dissolved in mixtures of these two solvents, say methyl alcohol and water, it was found that as the amount of one solvent, methyl alcohol for instance, decreased the methyl alcohol bands of the salt decreased in intensity, but did not change their position in the spectrum. At the same time the water bands of the salt became more intense. In the present work it is shown that the uranyl nitrate bands in pure water and in pure methyl alcohol occupy different positions. The problem to be investigated is to find out whether in mixtures of water and methyl alcohol the uranyl bands will show a gradual shift, or whether the methyl alcohol uranyl bands and the water bands will both exist together, their relative intensities being proportional to the relative amounts of methyl alcohol and water. It was found that the two sets of bands exist together and that the methyl alcohol bands decrease in intensity quite rapidly with increase of water. The blue-violet band showed marked changes until the amount of water reached about 20 per cent. In this work the amount of uranyl nitrate in the path of the light was kept constant, and the only variable was the relative amounts of methyl alcohol and water. The above would indicate that uranyl nitrate in water is "hydrated" and in methyl alcohol it is "alcoholated," and that the effect of "hydration" is much more persistent than that of "alcoholation." It is quite possible that this is due to the number of water molecules producing the hydration being greater than that of methyl alcohol molecules taking part in alcoholation.

(*f*) *Uranyl Nitrate in Ethyl Alcohol.*—The absorption of uranyl nitrate in ethyl alcohol was mapped and the general

[1] Carnegie Institution of Washington, Publication No. 110.

characteristics were found to be the same as for the water and methyl alcohol solutions. A new band was found at λ 5200 which was about 50 A. U. wide. All the uranyl bands were very faint and wide and therefore difficult to measure. There were deviations from Beer's law similar to those found for the methyl alcohol solution. On account of the diffuseness of the bands no spectrograms were made of mixtures of water and ethyl alcohol. Following are approximately the positions of a few of the bands:

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
λ	5000	4800	4630	4475	4325	4180	4080	3970	3875

(*g*) *Absorption Spectrum of Anhydrous Uranyl Nitrate.*—When it was first discovered that the uranyl nitrate "water" bands were all shifted to the violet with reference to the bands of the other uranyl salts in water, as well as with reference to the uranyl nitrate bands in other solvents, it was thought that possibly it was more hydrated than the other salts in solution. The uranyl salts crystallized from water solutions at ordinary temperatures have the following composition: $UO_2(NO_3)_2.6H_2O$, $UO_2SO_4.3H_2O$, $UO_2(CH_3COO)_2.2H_2O$, and $UO_2Cl_2.H_2O$. This fact would favor the supposition that in solution the nitrate might be more hydrated than the other salts. The fact that the absorption of the aqueous solution of the nitrate and the crystallized salt was very much the same, as far as the positions of the uranyl bands is concerned, also seemed to favor this view.

In this connection it was considered important to examine the absorption spectrum of the anhydrous uranyl nitrate. This salt was powdered and placed in a closed glass tube just above the slit of the spectroscope. The light of a Nernst glower was then focused upon the surface of the salt nearest the slit and an exposure of about three hours made. In this way we examine light that has penetrated a short distance into the powder and is then diffusely reflected.

The absorption spectrum was found to consist of quite a large number of bands which seem quite different in many respects from those of the solution. The following are the ap-

proximate wave lengths: $\lambda\lambda$ 4800, 4650, 4500, 4420, 4360, 4280, 4180 (broad), 4060 (broad), 3950 (broad), 3820 (broad), 3700 (narrow) and 3600 (narrow). The bands marked broad are from 50 to 60 A. U. wide and the narrow bands about 20 A. U. If the first band is the *a* band, then the bands of the anhydrous salt are to the violet of the corresponding bands of the crystals and of the solution. If it is the *b* band the opposite is the case. On account of the smallness of the intensity of the bands it could not be settled whether λ 4800 is the *a* or the *b* band. Further investigation of this point will be made.

There are two difficulties in the above theory, difficulties for which no explanation has thus far been suggested. In the work on the effect of rise of temperature on the absorption spectrum it was found that the uranyl nitrate bands did not shift to the red. On the other hand, the uranyl sulphate and uranyl chloride bands were shifted to the red under the same conditions. (In these cases aqueous solutions were investigated.) If the uranyl nitrate bands owe their position to a large amount of hydration it would be expected that with rise in temperature they would be shifted towards the red more than the bands of the sulphate and chloride. Another difficulty is that of the effect of dilution. The greater the dilution the greater the dissociation, and, therefore, according to the theory of Arrhenius, for very dilute solutions the UO_2 group should exist in the ionic condition and the absorption spectrum of all the salts should be the same, *i. e.*, the uranyl bands should then occupy the same positions independently of the kind of salt. No effect of this kind is to be noticed, as was shown above under the division describing the effect of dilution. It is intended to use much more dilute solutions in the future.

VI. Absorption Spectra of Uranyl Bromide, Sulphate and Acetate.

(*a*) *Uranyl Bromide in Water.*—In B, Plate V, we have the absorption spectra of uranyl bromide (crystalline salt, $UO_2Br_2.H_2O$). The exposures were 1 minute to the Nernst glower

with 0.8 ampere and a slit width of 0.08 mm., and a 3-minute exposure to the spark. The depth of the cell was 3 mm. and the concentrations were 1, 0.75, 0.5, 0.33, 0.25, 0.2 and 0.16 normal, the spectrum for the most concentrated solution being that next to the comparison scale.

It will be seen that uranyl bromide gives rise to an absorption very similar to uranyl nitrate, there being a blue-violet and an ultraviolet band. The absorption for the 1 N solution is complete for all wave lengths less than λ 4470. For 0.75 N the limits of the blue violet band are $\lambda\lambda$ 4450 and 3900, the ultraviolet band beginning at λ 3800. For 0.5 N the blue-violet band shows considerably large transmission, having almost completely faded out. Its middle comes at about λ 4250. The ultraviolet band gradually recedes towards the shorter wave lengths as the dilution increases.

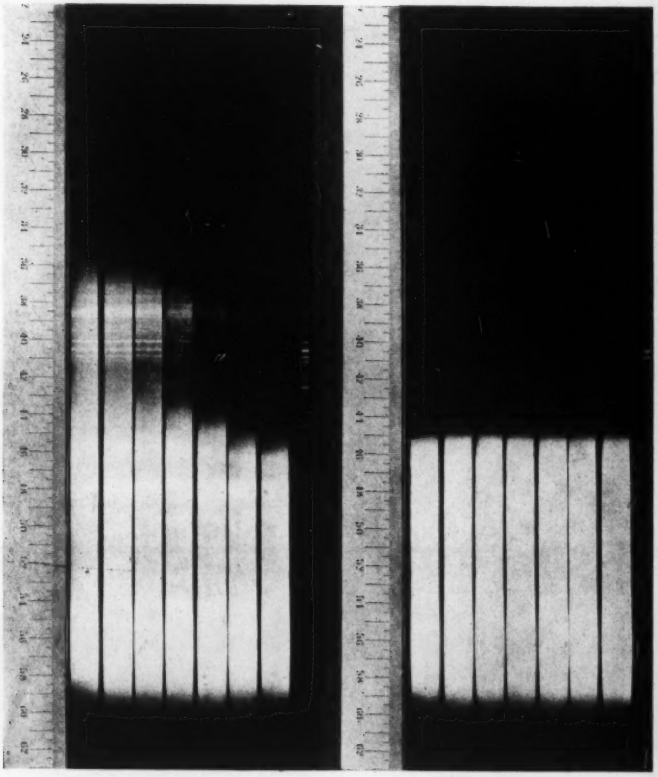
The uranyl bands themselves do not show nearly so prominently as in the case of the chloride and nitrate. The bands are very wide and diffuse. Their approximate positions are:

a.	*b.*	*c.*	*d.*	*e.*	*f.*
4880	4720	4560	4450	4280	4160

The spectrogram showing a series to test Beer's law is given in A, Plate V. The concentrations, beginning with the strip nearest the numbered scale, are 1, 0.75, 0.5 0.33, 0.25, 0.2 and 0.16 normal, the corresponding depths of cell being 3, 4, 6, 9, 12, 18 and 24 mm., respectively. Beer's law is found to hold, the limits of the absorption bands being independent of the above range of concentrations. The ultraviolet band and blue-violet band have a small region of transmission between them which shows in the original film but not on the print from it. This region of transmission is very faint and is quite a sensitive index to any possible deviations from Beer's law. It shows no changes in intensity with change in concentration. The uranyl bands *a* and *b* show although they are very indefinite. Concentration does not affect their intensity in the least as far as can be detected.

(*b*) *Absorption Spectrum of Uranyl Sulphate.*—The mapping

Plate V.



B A

of the absorption spectrum of uranyl sulphate in water showed that it was very much like that of the nitrate in water. As in the case of the nitrate the *i* band was much weaker than the adjacent bands. Beer's law was found to hold. The addition of a large amount of sulphuric acid was found to make the uranyl bands much sharper, but not to cause them to shift. Much more work will be done on the effect of strong acids on the uranyl bands. The following gives the wave lengths of the sulphate bands:

a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*j.*	*k.*	*l.*
4900	4740	4580	4460	4330	4200	4070	3970	3850	3740	3630	3530

(*c*) *Uranyl Acetate in Water.*—Uranyl acetate crystallizes from a water solution at ordinary temperatures as

$$UO_2(CH_3COO)_2 2H_2O.$$

The aqueous solution of this salt is very similar to that of the uranyl salts previously described, showing the blue-violet and ultraviolet bands and also the characteristic uranyl bands. This salt in solution is much more highly colored for the same concentration than the nitrate or bromide.

Plate VI, B, represents the absorption of a series of solutions where the concentration was kept constant and the depth of layer varied. The usual procedure was to keep the concentration constant and vary the depth of cell. For salts obeying Beer's law, this would give the same absorption as keeping the depth of cell constant and varying the concentration so that in our spectrograms of a salt where Beer's law holds, no difference is made between these two cases. Where Beer's law is deviated from, the two cases will not be identical. For the case under consideration the concentration was 0.031 N and the depths of cell, starting with the strip nearest the numbered scale, were 24, 18, 12, 9, 6, 4 and 3 mm. The length of exposure to the Nernst glower with 0.08 ampere and a slit width of 0.08 mm. was 1 minute.

The blue-violet band has the boundaries $\lambda\lambda$ 4500 and 4050 for a 24 mm. cell, and $\lambda\lambda$ 4400 and 4100 for a depth of 18 mm., the middle of the band thus coming at about λ 4250. The

long wave length edges of the ultraviolet band are $\lambda\lambda$ 3750, 3700, 3680, 3660, 3630, 3600 and 3580 for depths of cell of 24, 18, 12, 9, 6, 4 and 3 mm., respectively.

A photograph was made to bring out the small uranyl bands. An exposure was first made for 1 minute (0.08 ampere and 0.08 mm. slit) in the yellow end of the spectrum. This solution was 15 mm. deep in every case. The screen was interposed so as to cut off all light of greater wave length than λ 4450. A long exposure to the Nernst filament—about 5 minutes—was then made. Another screen was then interposed which cut out all light of wave length greater than λ 2800, and an exposure made to the spark. During these three exposures nothing was moved except the screen and thus the question of any mechanical moving of the photographic film was eliminated. From these two plates the positions of 9 uranyl bands were measured. These were as follows:

a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*
4910(?)	4740	4595	4455(?)	4310	4160	4070	3970	3865

It will be seen that these bands are all nearer the red than the bands of uranyl nitrate in water.

Deussen found the following values:

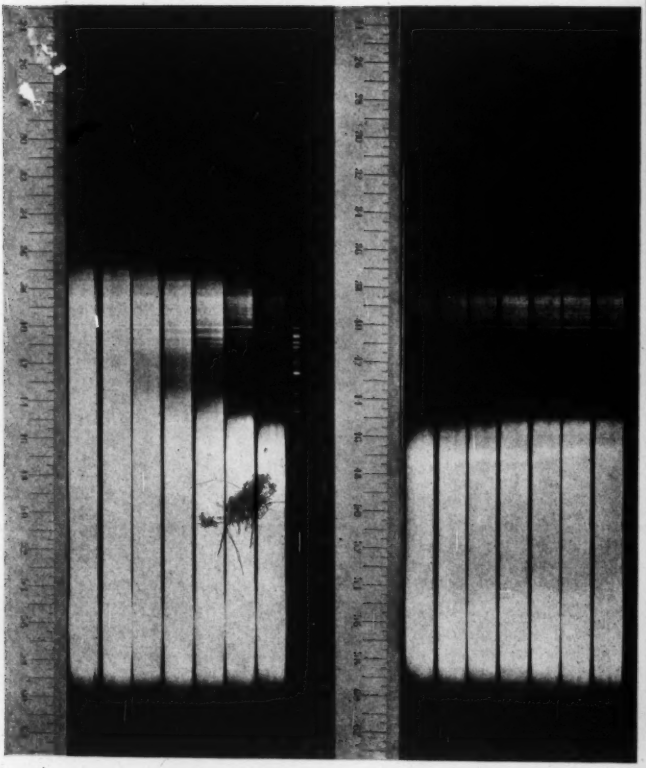
a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*j.*
4875	4730	4575	4420	4310	4180	4060	3950	3860	3770

These are in quite good agreement with the values given above.

The spectrogram A, Plate VI, represents change in absorption of uranyl acetate with concentration when the amount of salt in the path of the light beam is kept constant. The exposure was 1 minute to the Nernst glower, with 0.8 ampere (slit 0.08 mm.), and 3 minutes to the spark. Starting from the comparison spectra the concentrations are 0.25, 0.185, 0.125, 0.083, 0.0625, 0.042 and 0.031 normal, the corresponding depths of cell being 3, 4, 6, 9, 12, 18 and 24 mm.

This uranyl salt shows a deviation from Beer's law which is different from the deviation of any salt previously studied.

Plate VI.



B A

All other salts show, for a Beer's law series, a greater absorption at the greater concentration. Uranyl acetate shows the opposite, a greater absorption for the less concentrated solutions. For the 0.25 N solution the blue-violet band extends from λ 4150 to λ 4250. At 0.031 N it has broadened, so that its limits are $\lambda\lambda$ 4500 and 4050. This broadening of the absorption is gradual. In like manner the ultraviolet band extends to λ 4400 for the 0.25 N solution and to λ 4300 for the 0.031 N solution.

A 0.188 N solution of uranyl acetate 14 mm. in length was diluted to 0.007 N and 380 mm. in length. The absorption was found to be greater for the more dilute solution. The uranyl bands were not shifted and were much broader in the dilute solution.

(*d*) *Anhydrous Uranyl Acetate.*—To determine whether the water of crystallization of uranyl acetate, $UO_2(CH_3COO)_2 \cdot 2H_2O$, had any effect on the position of the uranyl acetate bands, the absorption of the anhydrous salt was found in the same way as for uranyl nitrate. Seven bands could be detected, but most of them were quite faint, although stronger than the bands of the nitrate:

a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*
4905	4775	4605	4460	4320	4200	4085

It will be seen that there is a slight shift towards the red as compared with the aqueous solution.

(*e*) *Uranyl Acetate in Methyl Alcohol.*—For the uranyl acetate the exposure to the Nernst glower, with 0.8 ampere and a slit width of 0.08 mm., was 1 minute. No exposure was made to the spark except for a comparison spectrum. Starting with the strip nearest the scale, the concentrations were 0.25, 0.20, 0.16, 0.12, 0.10, 0.07 and 0.06 N. The depth of cell was constant, 6 mm. The edges of the blue-violet absorption were as follows: 0.25 N, $\lambda\lambda$ 4550 and 3850, 0.20 N $\lambda\lambda$ 4520 and 3900, 0.16 N $\lambda\lambda$ 4500 and 3950, and 0.12 N $\lambda\lambda$ 4550 and 4000. The middle of the band would thus come

at about λ 4270. As the spark was not used the exact edges of the ultraviolet band cannot be given.

The uranyl bands had the following positions:

a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*
4875	4720	4585	4445	4320	4185	4070	3975

A plate was made to test Beer's law. Starting with the strip nearest the comparison scale the concentrations were 0.25, 0.20, 0.16, 0.12, 0.10, 0.07 and 0.06 N, the corresponding depths of cell being 6, 7.5, 9.5, 12, 15, 19 and 24 mm. The deviation from Beer's law is the same in direction as for uranyl acetate in water solution and is not nearly so great. For the 0.25 N solution the limits of the blue-violet band were $\lambda\lambda$ 4470 and 3925, the distance between the blue-violet band and the ultraviolet band at this concentration being about 100 A. U. units. For the 0.06 N solution the blue-violet and ultraviolet bands have completely merged and the limit of absorption is about λ 4600.

(*f*) *The Uranyl Bands of the Acetate.*—The following table gives the approximate wave lengths of the uranyl bands of the acetate in water and in methyl alcohol, and of the anhydrous powder.

Bands of Uranyl Acetate.

	a.	*b.*	*c.*	*d.*	*e.*
Water	4910	4740	4595	4455	4310
Methyl alcohol	4900	4770	4600	4460	4320
Anhydrous salt	4910	4760	4610	4460	4330

	f.	*g.*	*h.*	*i.*
Water	4160	4070	3970	3830
Methyl alcohol	4200	4090	....	....
Anhydrous salt	4190	4070	3980	....

From this table it seems that the positions of the bands of the acetate under these different conditions are about the same.

VII. The Phosphorescent and Fluorescent Spectra of Uranium.

Many bodies on being exposed to light, X-rays, α, β, γ or cathode rays, on being heated or rubbed, emit light. This is

generally called phosphorescence when the light is emitted after the stimulating agent ceases to act, and fluorescence when the excited light ceases to be emitted as soon as the exciting cause ceases. In general, liquids and gases fluoresce while solids phosphoresce. Some of the strongest phosphorescent compounds are the uranyl salts. These salts emit bands of phosphorescent light in the green region of the spectrum.

A considerable amount of work on the phosphorescence of uranyl compounds has been done by the Becquerels. E. Becquerel[1] found that the phosphorescent spectra of pure uranyl chloride and of double salts of uranyl and potassium or ammonium were quite different, and that apparently the presence of potassium and ammonium caused the bands to shift towards the longer wave lengths. The wave lengths of the bands as given by Becquerel are:

Phosphorescent Bands.

	1.	2.	3.	4.
Uranyl nitrate	6544	6180	{5810 / 5860}	5590
Uranyl acetate	6525	6180	5860	5590
Uranyl chloride	....	6230	5955	5685
Uranyl sulphate	6620	6262	5955	5690

	5.	6.	7.
Uranyl nitrate	{5325 / 5325}	5090	4920
Uranyl acetate	5325	5090	4920
Uranyl chloride	5433	5176	4980
Uranyl sulphate	5418	5170	4945

The bands of the nitrate and acetate come at about the same place in the spectrum, whereas the chloride and sulphate bands are farther towards the red. H. Becquerel[2] finds that at low temperatures the phosphorescent uranyl bands become quite sharp in the same way that absorption bands do. For uranyl nitrate he gives the following table:

[1] Ann. Chim. Phys., [4] **27**, 539–579 (1872).
[2] Compt. Rend., **144**, 459–462 (1907).

Phosphorescent Spectrum of Uranyl Nitrate.

Room temp.	Liquid air temp.	Room temp.	Liquid air temp.
6210–6150	6360	5360–5280	5327–5320(s)
	6175–6165		5303–5292(s)
	6145–6127		5272
	6104		5240
	6005–6045		5190
5940–5840	5860–5853(s)		5137
	5837–5830(s)	5120–5060	5115
	5782		5097–5090(s)
	5707		5074–5070(s)
	5630		5018
	5600		4975
5630–5550	5585–5575(s)		4925
	5558–5548(s)	4893–4855	4903–4896(*s*)
	5490		
	5435		
	5375		

Further work has recently been published by J. Becquerel and Onnes.[1] At the temperature of solid hydrogen the intensity of emission is not diminished and the bands which existed at liquid air temperatures undergo further subdivision. Lowering the temperature shifts the emission bands towards the violet. For instance, for the double sulphate of uranyl and potassium:

80° K	4904.2	5114.8	5342.4	5590.9	5863.1
20° K	4903.4	5113.5	5341.0	5588.9	5860.5
	0.8	1.3	1.4	2.0	2.6

The displacement of the phosphorescent bands caused by lowering the temperature from 20° to 14° is very small, and it is quite possible that as the temperature is lowered the bands approach asymptotically a limiting position. Becquerel and Onnes find that the difference in the appearance of the different groups of bands is the result of successive ascending changes in the relative intensities of the bands in these groups. They find, when crystals of double salts are used, that the spectrum depends more upon the acid of the salt than upon the other base. The differences between the frequencies of two suc-

[1] Commun. Phys. Lab., Univ. Leiden, Nos. 110, 111.

cessive homologous bands are practically constant, not only for the same, but also for all series of homologous bands of the same salt. The values of this constant for the various salts differ but slightly from one another.

At low temperatures the phosphorescent spectrum of uranyl compounds resembles that of the channeled spectrum of nitrogen and carbon. Becquerel and Onnes consider both to have the same character. Placing the phosphorescing uranyl salt in a powerful magnetic field did not produce any noticeable effect upon the uranyl bands. Some of the bands become arbitrarily absorption or emission bands, and at low temperatures the wave lengths are the same for both kinds of bands. Following is a table giving the wave lengths of the phosphorescent bands of various uranyl salts at 80° C.

The authors have done a little work on the phosphorescent spectra of uranyl compounds. For the stimulation of the phosphorescent bands either sunlight or the light from a spark has been used. The glass screens previously described or a Feuss monochromatic illuminator were used when only certain wave lengths of exciting light were needed. In the case of uranyl nitrate it was found that practically no phosphorescence was excited unless the exciting light had a wave length less than λ 4900. For all wave lengths less than this, phosphorescence was excited, but the bands seemed the same, irrespective of the wave length of the exciting light. It seems that the energy that is absorbed by the series of uranyl absorption bands is partly radiated as the energy of the phosphorescent bands. This suggests a number of lines of work which we hope to carry out in the future. Among these are the following: Are the phosphorescent bands of the salts of uranyl affected in the same way as the uranyl absorption bands? In the case of uranyl chloride can phosphorescent light be excited by the bands in the region λ 6000? Does light of wave lengths between that of the uranyl absorption bands excite phosphorescence? In the case of uranyl nitrate obtained from an alcoholic solution would light of wave length greater than λ 4900 excite phosphorescence?

Phosphorescent Bands.

Double sulphate of uranyl and sodium.	4891.5	5101.2	5330.0	5578.5			
	....	5125.4	5354.7	5604.6			
Double sulphate of uranyl and ammonium.	4912.6	5124.5	5355.4	5607.4	5881.1	6184.0	
	4934.7	5147.8	5380.1	5633.3	5908.0	6215.7	
Uranyl sulphate.	4918.3	5133.9	5369.4	5626.8	5910.1	6219.5	
	.....	5160.2	5395.8	5654.0	5938.8	....	
Uranyl nitrate.		5069.6	5301.5	5554.6	5832.9	....	
Double acetate of uranyl and sodium.	4732.5	4932.5	5148.6	5384.5	5642.7		
		4950.2	5167.8	5404.5	5663.4		
	4762.3	4964.9	5184.9	5424.0	5685.8		
	4769.2	4972.1	5192.2	5431.6	5694.6		
	4785.8	4990.2	....	....			
	4794.6	4999.2	5221.4	5463.5			

Different salts of uranyl phosphoresce very differently. The specimens of uranyl chloride gave very weak and diffuse bands. Uranyl nitrate obtained from the evaporation of a methyl alcohol solution showed no phosphorescence. Uranyl bromide also gave very little phosphorescent light on excitation. Using the Hilger spectroscope, the following approximate wave lengths for bands of various salts were found:

Uranyl sulphate	5660	5580	5420	5315
Uranyl nitrate	5670	5600	5410	5330
Uranyl acetate	....	5570	....	5340
Uranyl sulphate	5210–5160	5085	4950	4860
Uranyl nitrate	5180	5100	4970	4840
Uranyl acetate	....	5070	....	....

The bands are so hazy and wide that these measurements mean very little.

Very little has been done on the fluorescence of solutions of uranyl salts. Some work by Stokes,[1] Becquerel,[2] Morton and Bolton,[3] and others, treats of fluorescent bands. Morton and Bolton give the following wave lengths for some of the fluorescent bands of the solid salts:

Uranyl acetate, solid	6240	6070	5760	5500
" chloride, solid	6300	6000	5660	5400
" monophosphate, solid	6510	6170	5850	5600
" " in solution	6470	6200	5910	5650
" sulphate	6520	6150	5870	5600
" " anhydrous	6580	6230	5930	5630
Uranyl acetate, solid	5240	5030	....	....
" chloride, solid	5180	4930	....	....
" monophosphate, solid	5200	5100	4880	4720
" " in solution	5380	5160	4920	4800
" sulphate	5340	5110	4890	4770
" " anhydrous	5365	5145	4850	4780

VIII. The Absorption Spectra of Solutions of Uranous Salts.

Very little work has been done up to the present on the absorption spectra of uranous salts, largely because of their

[1] Phil. Trans., **1852,** II, 463; **1853,** III, 385.
[2] Ann. Chim. Phys., [3] **55,** 86 (1859); [3] **57,** 101 (1859); [4] **27,** 639 (1872).
[3] Chem. News, **28,** 47, 113, 164, 233, 244, 257, 266 (1874).

very unstable character in solution. J. Formánek[1] describes the absorption spectra of uranous chloride. This was prepared by adding a little zinc and hydrochloric acid to a uranyl chloride solution. He found that the spectrum changed as the uranyl chloride was being reduced. A very strong band was found at λ 6507. The other bands, eleven in number, were $\lambda\lambda$ 6722, 6367, 6165, 6030, 5782, 5497, 5238, 5064, 4962, 4840 and 4519.

A similar method has been used by the writers. The uranous nitrate, sulphate and chloride were formed by adding the corresponding acid to a solution of the uranyl salt containing some zinc. The uranous chloride and sulphate were quite stable in solution, remaining reduced for weeks. Uranous sulphate crystallizes out from solution as $U(SO_4)_2.9H_2O$. Solutions in alcohol can be reduced just as easily as solutions in water. Uranous nitrate was found to be very unstable. At the present writing a number of spectrograms have been made, and much more work will be done on these uranous salts and on the absorption spectra of the various oxides. It has already been found that uranous chloride has very different spectra in different solvents.

Uranous Sulphate.—Plate VII, A.—Only one spectrogram has as yet been made with uranous sulphate,

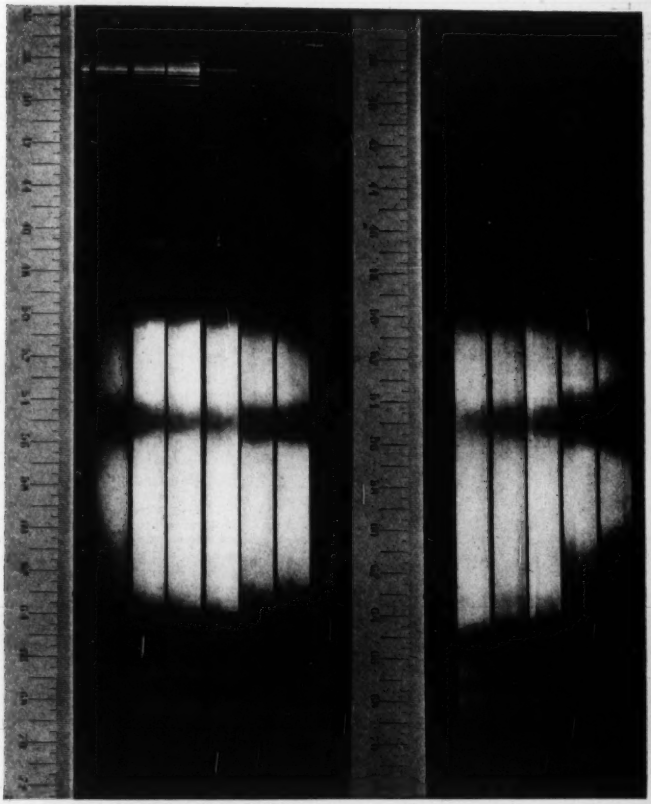
$$U(SO_4)_2.9H_2O,$$

in water. The bands are quite similar to the uranous chloride bands. The absorption in the blue and shorter wave lengths is complete. The following bands appeared: $\lambda\lambda$ 6700, 6500, 6300, 5480 and 4900. The 6500 band was the strongest of all and on increasing the depth of cell this widened out and, uniting with the 6700 and 6300 bands, formed one very wide absorption band extending over hundreds of Angström units. The 6300 band is very weak, the 6700 band somewhat stronger. The 5480 band is somewhat weaker than the 4900 band. On increasing the depth of cell these two bands widen enormously.

From a comparison of uranous chloride and uranous sul-

[1] Die qualitative Spektralanalyse, p. 99.

Plate VII.



B A

phate absorption spectra, it is seen that the relative intensities and positions of the bands for the two salts are the same.

A uranous chloride solution, Plate VII, B, was made by adding hydrochloric acid and metallic zinc to a normal uranyl chloride solution. In a short time the solution became very green in color and gave the characteristic uranous spectrum. Besides the bands above described for the sulphate there appeared three very strong bands in the blue-violet region, $\lambda\lambda$ 4600, 4770 and 4970. The other bands, $\lambda\lambda$ 5520, 6350, 6530 and 6750, were the same as for uranous sulphate previously described.

To a 0.25 normal solution of uranyl chloride in methyl alcohol was added a small amount of hydrochloric acid and zinc. This reduced the yellow uranyl chloride to the green uranous chloride. The absorption spectrum, Plate VIII, B, of uranous chloride in methyl alcohol was found to be different from that of the same salt in water. Bands closely resembling the bands in water appeared at $\lambda\lambda$ 4600 and 4780. The water band, λ 4970, was broken into two bands in methyl alcohol, $\lambda\lambda$ 4930 and 5030. In the alcohol there was a very broad weak band at about λ 5300. This did not appear at all in aqueous solution. The band at λ 5580 is quite like the water band. Weak and broad alcohol bands appear at $\lambda\lambda$ 6150, 6300, 6480. A strong band appears at λ 6750. As the depth of the alcoholic solution is increased the widening of the bands is quite unlike the widening of the water bands with increased depth of layer.

In this plate (B, Plate VIII) the three lower strips represent the absorption spectra of uranous chloride in methyl alcohol, and the upper strip is made to show the difference between this and the absorption of a solution of uranous chloride in water.

A, Plate VIII, represents the absorption of uranous chloride in water, the depth of cell being varied.

The alcohol bands $\lambda\lambda$ 4600 and 4780 and 5580 are slightly shifted towards the red with reference to the analogous water bands.

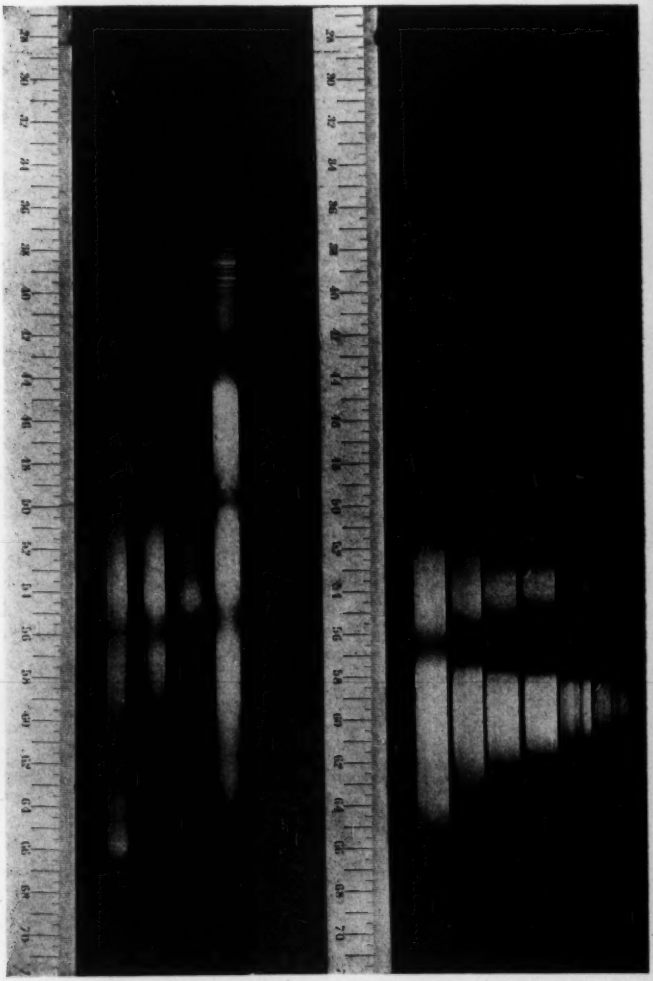
To a solution of uranyl chloride and calcium chloride in water some hydrochloric acid and a little metallic zinc were added. The absorption spectrum of this solution was very similar to that of the water solution of uranous chloride except in the blue and violet part of the spectrum. In this region there was an almost general transmission. A broad diffuse band appeared at λ 4300, and a very weak band at λ 4600. The other bands had about the same relative intensity and position as the pure water bands.

IX. The Various Uranium Spectra.

Plate III, B, was made under the usual conditions of slit width and integral intensity of the penetrating light beam. Starting with the strip next the numbered scale, the absorption spectrum is that of (1) a normal aqueous solution of uranyl sulphate 3 mm. thick; (2) a 0.25 normal aqueous solution of uranyl acetate 12 mm. thick; (3) a 0.75 normal aqueous solution of uranyl nitrate with 3 mm. depth of cell; and (4) 0.75 normal aqueous solution of uranyl sulphate, 4 mm. thick. The plate shows the greater relative absorbing power of uranyl acetate, the broadness of the uranyl bands of the acetate and also the fact that the uranyl bands of the nitrate are further towards the violet than the corresponding bands of the other salts.

Collecting the data for the various salts in different solutions we have the following:

Plate VIII.



B A

Uranyl Bands.

	a.	*b.*	*c.*	*d.*	*e.*	*f.*	*g.*	*h.*	*i.*	*j.*	*k.*
Chloride in water	4920	4740	4560	4460	4415	4170	4025	....	....	....	....
Chloride in methyl alcohol	4930	4760	4610	4465	4345	4220	4090	3980	3860	3760	....
Chloride in ethyl alcohol	4900	4750	4580	4400		4250	4100	3980	3860	....	....
Chloride and calcium chloride in methyl alcohol	....	4760	4590	4420		4260	4120	4010	....	....	....
Bromide in water	4880	4720	4560	4450	4280	4160	....	....	....	....	....
Sulphate in water	4900	4740	4580	4460	4330	4200	4070	3970	3850	3740	3530
Nitrate in water.	{4890 4800}	{4742 4722}	4540	4390	....	4155	4030	3905	3815	3710	3515
Nitrate in methyl alcohol	4930	4760	4610	4460	4325	4190	4070	3970	3855	....	....
Nitrate in ethyl alcohol	5000	4800	4630	4475	4325	4180	4080	3970	3875	....	....
Acetate in water	4910	4740	4595	4455	4310	4160	4070	3970	3865	....	....
Acetate in methyl alcohol	4900	4770	4600	4460	4320	4200	4090	3975	....	....	....

Bands of Some Uranous Salts.

Uranous and aluminium chlorides in water	6730	6530		5510		
Uranous and calcium chlorides in water	6740	6520		5500	4950	{4720 4570
Uranous chloride in methyl alcohol	6750	6480	{6300 6150 6080 5900}	5570,5300		
Uranous chloride in ethyl alcohol	6790	6535	6340	5610	4920	....
Uranous nitrate in water	6700	6470	....	....	....	....
Uranous sulphate in water	6730	6550	....	5500	....	....

It is a fact that investigations on the spectral emission and absorption of bodies have been far less fruitful in extending our knowledge of the structure of the atom than had been expected. This is largely owing to the almost infinite complexity of the structure of the atom and our general ignorance of the forces that exist there. Probably the best known example is that of the uranyl group which we have been describing. Let us consider the spectral vibrations that can be produced by components that exist or may be produced from the apparently simple UO_2 group: (1) We have the absorption spectrum described above. At low temperatures most of these bands break up into much finer bands. (2) The uranyl salts under various methods of excitation emit a phosphorescent spectrum of a large number of rather fine bands throughout the visible region of the spectrum. It is quite possible that this spectrum is intimately connected with that of the absorption spectrum. (3) We have the absorption spectrum of the uranous salts which has been described above. This spectrum has been probably caused by the change of valency of the uranium atom. Uranium is known to form quite a large number of oxides and it is quite possible that for each valency of the uranium we have a characteristic spectrum. (This also is being investigated.) It is also quite probable that at lower temperatures those spectra would consist of quite fine bands. (4) We have the spark spectrum and the absorption spectrum of oxygen, and (5) that of ozone which bears no relation to that of oxygen. (6) There is the exceedingly complex spark spectrum of uranium consisting of thousands of fine lines and also (7) the complex arc spectra. From radioactive experiments it is known that uranium is continually breaking down into ionium. (8) Ionium possesses the properties of a chemical atom and most likely has a spectrum of its own. This would make eight spectra. (9) Ionium breaks down into the radium and radium has a very characteristic spark spectrum, as does also (10) the radium emanation. During the various radioactive transformations several α-particles are emitted with a velocity almost as great as that of light. It is probable that these particles are mov-

ing with very great velocities in the uranium atom under ordinary conditions. (11) The α-particles are known to be charged helium atoms and therefore under proper excitation would give the helium spectrum. The radium emanation breaks down into radium A, B, C, D, E and F. These products behave like chemical elements and probably have characteristic spectra. (12) The final product is lead, which has very complex spark and arc spectra. During these transformations several electrons have been thrown off from the various products with enormous velocities. In a very large number of the above spectrum lines the Zeeman effect indicates the presence of negative electrons and charged doublets.

We thus see what an extremely complex system the group UO_2 must be, and it might seem almost hopeless to disentangle the mystery of its various spectra. At present we know that the arc and spark spectra problem is very complex and that we have very few methods of producing any changes in them. Practically the only method of changing the frequency of these vibrations is by applying a very powerful magnetic field or great pressure and these changes in the frequency are very small. One very important result, however, has been obtained by Kayser, Runge, Wood and others. This work consists in separating spectrum lines into various series. A series of lines are those whose intensity and Zeeman effect vary in the same way when the conditions outside the atom are changed. The work of Wood is important as showing that spectrum lines are due to different systems of vibrators inside the atom. By using monochromatic light of different wave lengths he has been able to excite different series of lines which constitute altogether the fluorescent spectrum of the element.

Present theories of the atom usually regard the electrons and other vibrators that are the sources of arc and spark lines as being well within the atom and as affected by external physical conditions only under very special circumstances. Stark believes that these electrons may rotate in circular orbits, the locus of the centers of these orbits being a closed curve, say a circle. This system will be equivalent to a positive or negative charge according to the sense of rotation of

these electrons. These electrons we will call ring electrons. Supposing these systems to be positive charges, it will require electrons to neutralize these charges. Several of these neutralizing electrons may be in the outer parts of the atom and under certain conditions might be knocked off from the atom. These easily removable electrons will be called "valency" electrons, and can exist under different conditions of "looseness" of connection with the atom. Most of the neutralizing electrons will probably lie far within the atom. For instance, we would expect that in the uranium atom the charged helium atoms are neutralized by negative electrons.

Our theory is that the finer absorption bands of such salts as neodymium, erbium and uranium are due to vibrations of these neutralizing electrons, and that the forces acting upon these are considerably different from those acting on the ring electrons, which, in many cases, give a normal Zeeman effect. It is probable that these neutralizing electrons play the greatest rôle in the optical properties of bodies, such as the properties determining the index of refraction, the extinction coefficient, etc.

Usually the equation of motion of such an electron is given by an equation like the following when a light wave of an electric field $E \cos pt$ is passing by it:

$$m\frac{d^2x}{dt^2} + k\frac{dx}{dt} + n^2x = E \cos pt,$$

where m is the total mass (electromagnetic and material) of the electron, $k\ dx/dt$ is the damping or frictional term and n^2x is the quasi-elastic force. It is an experimental fact as shown by the above work and the work of other investigators, that k and n^2 are not only functions of the electron and the atom, but that they are also functions of the physical and chemical conditions existing in the neighborhood of the atom.

On the other hand, the effect on k and n^2 for a ring electron, when external physical and chemical conditions are changed, is very small. It is for this reason, and the probable fact that there are relatively few neutralizing electrons, that we

believe that much greater progress can be made in determining some of the properties and constitution of various interatomic systems of atoms and molecules by the study of the absorption spectra of uranium and neodymium than by a study of the arc or spark spectra of the same.

The method of attacking the above problem will be to study the effect on the spectra of a body produced by changing the physical and chemical conditions about the light absorbers or emitters within as wide ranges as possible. Some of the possible changes that can be made are as follows: Take for instance the uranyl group UO_2. We can find the effect upon the absorption bands produced (1) by diluting the solution, (2) by changing the acid radical to which the uranyl group is united, (3) by changing the solvent and using mixtures of solvents, (4) by adding other salts (like aluminium chloride), or (5) by adding acids of the same kind as that of the salt of the uranyl group. The effect (6) of adding foreign salts and acids at the same time and then varying the solvent, or the temperature, can also be tried. In this way a very large number of very interesting things can be tested. In most of these changes *lc* will be kept constant.

In the above example the temperature (7), the external pressure (8), the electric field (9) and the magnetic field (10) can be changed between wide limits. The latter effect is a very important one. For example, in aqueous solution neodymium salts give a large number of fine bands, in glycerol there are quite a number of new bands replacing the "water" bands, and in the alcohols there are various "alcohol" bands. At low temperatures these bands become very fine and it is quite possible to detect the Zeeman effect. Now it seems quite probable that a "glycerol" band and an "alcohol" band that seem to replace each other as the solvent is changed are both due to the same vibrator. If the Zeeman effect is the same in both cases it would be a strong argument in favor of the above theory. A case that will soon be described is very important. It was found that the wave lengths of certain neodymium lines in a pure water solution did not change when the temperature was raised from 0° to 90°. If, how-

ever, calcium chloride was added, then on raising the temperature the above bands were shifted to the red. A very interesting and important investigation is whether the Zeeman effect on the band would be affected by the presence of substances like calcium chloride.

To be compared with the above changes are changes in the absorption spectra of the crystals of the salt (11) as affected by water of crystallization, or by the presence of foreign substances, or as affected by the polarization (12) or direction of passage of light through the crystal. The absorption spectra (13) of the anhydrous powder at different temperatures, etc., should be found. The phosphorescent spectrum (14) should be studied in this connection, especially as affected by the mode of stimulation (X-rays, cathode rays, heating or monochromatic light of different wave lengths). The temperature, electric or magnetic field could be changed about the phosphorescing body. The effect of change of state (15) should be tried if this is possible, also any possible changes of valency of the atoms (16) composing the body investigated. We shall attack the problem from all of these standpoints.

After correlating the data obtained by the above named investigations it is pretty certain that it will be possible to take each vibrator and trace the effects produced upon it by the above changes. It is also quite certain that we shall also know something of the nature of the vibrating system and the part that it plays in that complex body we call the atom.

For instance, let us take the bands of uranyl nitrate. It was found that the uranyl bands of an aqueous solution of the nitrate had shorter wave lengths than that of any other uranyl salt in water. The uranyl bands of the nitrate in other solvents were farther towards the red than the bands of an aqueous solution. Now although the solvent has a great effect upon the bands, nevertheless it seems quite certain that the NO_3 group has a very considerable effect upon the vibrations of the uranyl group. If it were possible to find the ratio e/m for the vibrators in this case by the Zeeman effect, it might be possible to find an approximate value for the force exerted by the NO_3 group upon the vibrator. It seems quite

certain that this force differs for the vibrators producing different bands. The measurements of the wave lengths of the uranous bands are as yet very few, yet they seem to indicate that for aqueous solutions of the uranous salts, the bands of the nitrate are farther towards the violet than the bands of the other uranous salts. The values given for the phosphorescent bands by E. Becquerel (p. 73) and by J. Becquerel (p. 74) indicate that the bands of the nitrate are further towards the violet than those of the other uranyl salts. We thus see that throughout these three spectra the NO_3 group exerts a similar force upon the vibrators that are the cause of the bands.

X. The Absorption of Neodymium Chloride in Glycerol and in Mixtures of Glycerol and Water.

The absorption spectrum of a glycerol solution of neodymium chloride is much like that of the aqueous solution in its general characteristics, but when proper concentrations are used so as to bring out the fine bands it is found that the two spectra are entirely different. For example, the aqueous solution shows a very fine band at λ 4274. In the glycerol there is a band that on first sight appears to be exactly identical with this λ 4274 band. However, its wave length is about λ 4287, and it has two extremely fine components on each side, one at λ 4273 and one at about λ 4300. The same is true throughout the spectrum.

In general, in mixtures of water and glycerol the appearances indicate that there are "glycerol" bands and "water" bands and as the amount of one solvent is increased, so are the bands corresponding to this solvent increased in intensity. Herein lies a very large field for investigation and considerably more work is being carried on here along these lines. The above described spectrum of the glycerol solution of neodymium indicates that glycerol has a very great influence upon the vibrations of the electrons within the neodymium atom, and that this is due to a kind of "atmosphere" of glycerol about the neodymium atom. Jones and Anderson showed that alcohol has a similar effect, and that the "alcohol" bands

were much less persistent than the water bands. Further work is being done on the relative persistence of "water," "alcohol" and "glycerol" bands; also on the effects of foreign substances and rise of temperature on these bands, both in the pure solvent and for mixtures of solvents.

XI. Summary.

The absorption spectra of the uranyl salts contain a series of bands in the blue and violet. Twelve of these bands can usually be detected for each salt. Starting from the blue end of the series the bands are designated by the letters *a*, *b*, *c*, etc. These bands are usually diffuse and from 30 to 50 A. U. wide.

The uranyl bands of uranyl nitrate in water are all farther to the violet than the uranyl bands of any other salt investigated, or of uranyl nitrate in other solvents.

The uranyl absorption bands of crystals of uranyl nitrate agree with the absorption bands of an aqueous solution of the nitrate, with the exception of the *f*, *g*, *h* and *i* bands, these latter being shifted to the red in the crystal.

Dilution within the ranges studied does not affect the position of the uranyl bands. Theoretically, all the uranyl salts in water should give the bands of the same wave lengths for very dilute solutions.

The uranyl bands of the nitrate in methyl alcohol are all shifted to the red about 50 A. U. with reference to the bands in water. Mixtures of water and methyl alcohol show that we have both sets of bands existing for the same solution, the "water" bands increasing in intensity as the amount of water increases. The water bands are the more persistent. This indicates the existence of a hydrate and an alcoholate of the uranyl group. In ethyl alcohol the *a*, *b*, *c* and *d* bands are shifted to the red with reference to the methyl alcohol bands. The other bands appear to have the same positions as the methyl alcohol bands.

The absorption spectrum of the anhydrous salt is very complex and the bands could not be recognized.

The bands of uranyl bromide in water, of uranyl acetate in

water and methyl alcohol, and also of the anhydrous salt, are approximately of the same wave lengths, differing but slightly from the wave lengths of the uranyl nitrate bands of an aqueous solution.

The bands of uranyl sulphate in water are all shifted towards the red about 50 A. U. with reference to the uranyl nitrate bands in water. For both the sulphate and nitrate in water the bands are very much alike. The *i* band is very weak in both cases.

Uranyl chloride bands of an aqueous solution are shifted to the red with reference to the uranyl nitrate bands of an alcoholic solution. The addition of calcium chloride or aluminium chloride is found to produce very marked effects upon the uranyl chloride bands. The addition of sufficient aluminium chloride to a water solution of uranyl chloride, or of calcium chloride to a methyl alcohol solution of uranyl chloride, is found to cause the *d* and *e* bands to come together, so as to form a single wide band, and to cause the other uranyl bands to shift so that the whole resulting series of bands is almost identical with the series of bands of an ethyl alcohol solution of uranyl chloride. The effect of adding foreign substances also greatly modifies the intensity of the bands. An example of this difference of action is the effect of adding aluminium chloride to an aqueous solution of uranyl chloride. The *a* and *b* bands are affected entirely differently, the *a* band being very much reduced in intensity and made narrower, whereas the *b* band becomes very much stronger and wider.

A new set of fine bands in the green has been discovered in the absorption spectrum of an aqueous solution of uranyl chloride. These appear only for pure water solutions, a small amount of aluminium or calcium chloride causing them to vanish. They do not appear for methyl or ethyl alcohol solutions, nor for any other uranyl salt except very faintly for the sulphate.

The absorption spectrum of several uranous salts has been photographed. The spectrum is entirely different from that of the uranyl compounds. The absorption spectra of uranous chloride in methyl alcohol and in water were found to be very

different. The absorption spectrum of neodymium chloride in glycerol was found to be entirely different from that of the salt in water. For mixtures of water and glycerol there are indications of the existence of both sets of bands in the same solution. The "glycerol" bands are more persistent than "alcohol" bands with reference to water bands. Work is now being done on the relative persistencies of the various water, alcohol, glycerol, etc., bands.

The intensity of the phosphorescence of the same uranyl salts, obtained from different solvents by evaporation, is found to be very different. Monochromatic stimulation fails to excite phosphorescent bands until the wave lengths reach the region of the uranyl bands.

It is found that the NO_3 group has a very great influence on the frequency of the uranyl bands of absorption, of the uranous absorption bands and of the uranyl phosphorescent bands.

(The second part of this paper will be published in the February number of THIS JOURNAL.)

NOTE.

PECAN OIL.

This oil was prepared from the large cultivated pecans, which were kindly furnished us by Mr. E. Risien, of Rescue, Texas. The kernels made up 47.0 per cent. of the nuts, and contained 70.4 per cent. oil. The oil was extracted with ether, the ether evaporated, and the oil dried and filtered. It had a light straw color and a pleasant pecan odor and taste. The methods of examination are those described in Benedict and Lewkowitsch's "Oils, Fats, and Waxes." The figures given are the average of two determinations, as a rule. For purposes of comparison, the constants of olive oil, taken from the book referred to above, are given:

	Pecan oil.	Olive oil.
Specific gravity 15/15° C.	0.9184	0.916–0.920
Saponification value	198.0	185–196
Iodine absorption (Hübl's method)	106.0	77–88
Volatile acids (Reichert–Meissl value)	2.2	0.3
Acetyl value	1.16	.....
Insoluble fatty acids, per cent. (Hehner value)	93.4	95
Lecithin, per cent.	0.5	.....
Cholesterol, per cent.	0.28	0.46–1.00

The lead soap prepared from the fatty acids of this oil was completely soluble in ether, indicating the absence of saturated acids. Exposed to the air at room temperature, the oil gained 0.7 per cent. in weight in three days, after which it lost slightly. In a steam oven the oil gained in weight 0.65 per cent. in 4 days, after which it lost weight. As the oil had been previously freed from ether in a steam oven these values for oxygen absorption are probably low, but the oil evidently belongs to the nondrying class. Pecan oil resembles olive oil closely excepting in its iodine absorption value, which is near to that of beechnut oil or of cotton seed oil.

Calculated from the iodine value, the oil contains 24 per cent. linolin and 76 per cent. olein. But the fatty acids precipitated from the alkaline soaps with acid were solid at the room temperature, and altogether they melted in time, and when once melted did not solidify easily, yet it appears that this oil could not contain the amount of olein stated above, but must contain some other glyceride of a fatty acid having a higher melting point.

With the elaidin test a butterlike mass was formed which was not as solid as that obtained from olive oil.

TEXAS EXPERIMENT STATION. A. C. DEILER AND G. S. FRAPS.

REVIEWS.

THE CHEMICAL CONSTITUTION OF THE PROTEINS. By R. H. ADERS PLIMMER, D.Sc., Assistant Professor of Physiological Chemistry in, and Fellow of University College, London. In two parts. London, New York, Bombay and Calcutta: Longmans, Green & Co. 1908. Part I, pp. xii + 100, price, $1; Part II, pp. xi + 66, price, 80 cents.

This essay forms a part of the admirable series of monographs on Biochemistry now being issued under the editorship of Messrs. Plimmer and Hopkins. "The Chemical Constitution of the Proteins" is naturally one of the most important of the various topics which are under consideration and this difficult subject has been admirably treated by Dr. Plimmer in the present volumes. The first part deals with the chemical composition of the protein molecule and of the numerous amino-acid units that are comprised in it; the second part is devoted to a consideration of the various syntheses of protein-like substances which have been successfully accomplished by Curtius, Abderhalden, and above all, by Emil Fischer.

The writer is acquainted with no account in the English language of the chemistry of the proteins comparable either

for completeness or accuracy with the one under review and the monograph should be of great value to a large number of organic chemists who wish for a presentation from a strictly chemical point of view of so important a subject.

FIRST PRINCIPLES OF CHEMICAL THEORY. By C. H. MATHEWSON, PH.D., Instructor in Chemistry and Metallography at the Sheffield Scientific School of Yale University. First Edition. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1908. pp. vii + 123. Price, $1.

The contents of this volume are as follows: Natural classification of the elements; determination of molecular weights; determination of atomic weights; calculation of formulas; osmotic pressure and related phenomena with particular reference to dilute solutions of acids, bases and salts; the electrolytic dissociation theory; the law of chemical mass action; heterogeneous equilibrium and phase rule; thermochemistry. The author's treatment of these subjects is thoughtful and thorough; the book should be helpful to students as a reference book or for careful study of theory, as much of the theoretical matter scattered through the pages of larger text-books is here condensed.

The author says in the preface that the book is for the use of first year students at the Sheffield Scientific School, as reference text in connection with a six weeks' course on chemical theory which immediately follows the first four months' instruction in general chemistry. Probably most teachers who examine the book will prefer to postpone its use until the student has completed the work of the first year. E. R.

INTRODUCTION TO THE RARER ELEMENTS. By PHILIP E. BROWNING, PH.D., Assistant Professor of Chemistry, Kent Chemical Laboratory, Yale University. Second Edition. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. pp. x + 207. Price, $1.50 net.

It is seldom that the second edition of a well-known book is so broadened and enlarged and withal improved as is the case with this work of Dr. Browning. It is almost as if an entirely new treatise had appeared and we may well be glad that it is printed in the English language, for we have sadly needed an available book for student reference and use. These rarer elements, too often neglected in the curricula of our colleges and universities, can no longer be passed over for lack of an available text. By its appearance encouragement is sure to be given to study in this charming section of inorganic chemistry and even chemists who are no longer students might well perform many of the well chosen experiments and increase their knowledge at first hand of these elements of which we all know too little. Dr. Browning has

done his work well. The book covers 206 pages of description and experiments. Only lists of chief compounds are given and it is to be hoped that in future editions enlargement may be along the line of description of these compounds, their relative solubilities, etc. The methods of separation can, at least in most instances, be depended upon as the latest and best. To the reviewer the chapter on the rare earths is especially worthy of mention for its clearness of diction, its list of mineral sources, its classification and for carefully selected and described methods of separation. The chapter on the rare gases of the atmosphere and the chapter written by Dr. Boltwood on the radioactive elements are worthy additions which give the book completeness and added value, and the inclusion on the final pages of the qualitative scheme of separation of these rarer elements of Noyes, Bray and Spear, and that of Böhm, will give ready reference to these latest and best identification methods.

It is seldom that the reviewer has a pleasanter task than this book affords, for there is so little to criticize and so much worthy of praise. The book should be in the hands of every chemist.

CHARLES L. PARSONS.

GLASS MANUFACTURE. BY WALTER ROSENHAIN, B.A., B.C.E., Superintendent of the Department of Metallurgy and Metallurgical Chemistry at the National Physical Laboratory, New York. D Van Nostrand Co., 1908. pp. ix + 264. Price, $2.

Hitherto it has been difficult for general students to get the kind of information desired about glass. In the textbooks of technical chemistry the information is too meagre, in the larger books too diffuse and too much specialized. This present book supplies this want. Mr. Rosenhain is an expert, and writes a very interesting book, and writes it for the users, not for the makers of glass.

The book describes the chemical and physical properties of glass, raw materials, crucibles and furnaces, the various processes, bottle glass, blown and pressed glass, plate glass, crown glass, colored glass, optical glass, the theoretical requirements of optical glass and the attempts to meet these requirements by the work of Abbé and Schott of Jena. The account of the Jena glasses is particularly interesting. Mr. Rosenhain's book should find plenty of readers as it is the only one of the kind.

E. R.

DIE LACK UND FIRNISFABRIKATION. von PROFESSOR MAX BOTTLER, in Würzburg. Mit 29 Abbildungen im Text. Halle a/S.: Verlag von Wilhelm Knapp. 1908. pp. ix + 130. Price, M. 4.50.

This is a little book of about 40,000 words, covering the

whole subject of oil-varnish, oleo-resinous and spirit varnishes, their components and manufacture. It is necessarily brief and incomplete, but is designed to give information of materials and processes which are up to date, at least in Germany. It is not a book of formulas. After a few introductory pages, chiefly of definitions, materials used in varnish-making are described; one-fourth of the book is devoted to resins and the like, including such widely varying substances as rubber, camphor, spermaceti and pyroxylin, a brief, but on the whole, satisfactory chapter; the classification of copals is open to criticism, but probably no one could make such a presentation which would not be; it is really about time for those interested to get together and agree on some standards, no matter how arbitrary they may seem. As it is, every one is a law unto himself. Brief notices of drying oils follow, amounting to half a dozen pages. The statement is made that flaxseed contains 60 per cent. oil and yields by ordinary hot-pressing 28 per cent. As a matter of fact, the oil content varies from 37 per cent. (South American) to 42 per cent. (Calcutta), and the actual yield is from 32 to 33 per cent. While some German writers give the actual yield as low as 26, this is based on an estimate of about 37 per cent. total oil in European seed, so that on this point the author must be in error. Eight pages are given to turpentine, alcohol and other volatile solvents; lead and manganese compounds (catalyzers) are briefly described; then nearly half the book is given to apparatus and processes. This is illustrated with many pictures, most of them of apparatus now in use, of much interest; and the whole chapter will repay careful reading, being, in fact, open chiefly only to the objection that it is incomplete, which applies to the whole book. Spirit varnishes have relatively more space than others, and this chapter is especially good. There is a short section on bleaching and filtering. The book contains comparatively few references, but shows familiarity with recent work; it is for the casual student and the general reader, and such will find it useful and interesting.

A. H. SABIN.

ELECTRO-METALLURGY. By JOHN B. C. KERSHAW. With 61 Illustrations. New York: D. Van Nostrand Co. 1908. pp. xv + 303. Price, $2.

The author states in his preface that the book has been prepared for readers who have but a slight acquaintance with chemistry and electricity. The aim must be therefore to cover the ground in a general way, and to make the reading pleasant and attractive. This the author has done well; he

has described briefly the leading processes and has given the principal facts about the foremost plants so far as they are generally known; he also holds the interest of the reader. The book covers the metals aluminum, silver, gold, copper, iron, lead, nickel, tin and zinc; the elements calcium, magnesium, phosphorus, silicon and radium; it also discusses calcium carbide and acetylene gas, carborundum, glass, quartz-glass, graphite, carbon bisulphide and tetrachloride, and diamantine. Thus subjects are dealt with which lie outside of the usual range of electro-metallurgy. There are a few slips here and there, but the whole is accurate in the subjects with which the reviewer is familiar. Within the lines drawn by the author, the book will prove eminently satisfactory.

H. O. HOFMAN.

RAPID METHODS FOR THE CHEMICAL ANALYSIS OF SPECIAL STEELS, STEEL-MAKING ALLOYS AND GRAPHITE. By CHARLES MORRIS JOHNSON, Chief Chemist to the Park Steel Works of the Crucible Steel Company of America. New York: John Wiley & Sons; London: Chapman & Hall, Ltd. 1909. pp. vii + 221. Price, $3.

The author in his preface calls attention to the accounts of the methods which he originated and the investigations which he pursued to simplify and expedite the analysis of special steels and steel-making alloys. For this work he certainly deserves great credit, especially for the modifications he suggests in the method for the direct determination of nickel in steel and for the method for the determination of phosphorus in ferro-vanadium. In the former method the direction to use a 20 per cent. solution of potassium iodide is probably a misprint. The qualitative tests for the presence of vanadium, chromium, tungsten, and molybdenum in steels are useful and practical. It is impossible within the limits of an ordinary review to criticize the methods in detail, but it may be remarked that many of those described for the analysis of pig irons and ordinary steels are not the methods generally considered the most accurate. The method for the volumetric determination of manganese is neither as accurate nor as rapid as the bismuthate method, and the volumetric method for sulphur with an admitted variation of 25 per cent., while it undoubtedly has its sphere of usefulness, is not apt to be accepted by the buyer and seller of pig iron, as suggested by the author, however well its limitations may be understood.

Kopp's method for the determination of molybdenum in molybdenum powders is to be preferred to either of the methods given in this book, and Gooch's modified method

for the determination of titanium is far preferable to the one here recommended.

In the manipulations described in great detail the directions to wash a precipitate 40 or 50 times do not seem to make for rapidity, although this may be necessary when the precipitate is mixed with 50 cc. of paper pulp. Apart from the methods themselves the descriptions are usually clear and easily followed, but the departures from the strict rules of grammatical construction are frequent, and the constant use of what may be called "chemical slang" is really distressing. Such expressions as "evaporate to a scum," "wash free from chloride test," "evaporate the samples to fumes," do not seem suitable in a work of this character.

ANDREW A. BLAIR.